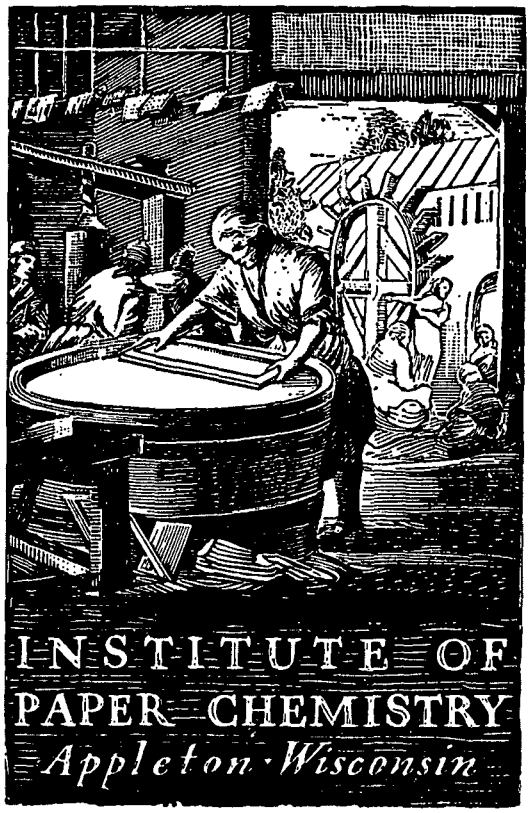
Project 3092 #1



A STUDY OF OXYGEN – PEROXIDE BLEACHING PROCESSES

Project 3092

Report One

A Progress Report

to

MEMBERS OF GROUP PROJECT 3092

October 5, 1973

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

A STUDY OF OXYGEN-PEROXIDE BLEACHING PROCESSES

SUMMARY

A kinetic study of the consumption of oxygen by pulps during oxygen bleaching shows a very complicated behavior which evades simple analysis. During the initial stages (up to 30 minutes reaction in some instances), the consumption of oxygen is proportional to the concentration of hydroxyl ion, the concentration of the applied caustic, and to the oxygen pressure. The dependence upon these parameters diminishes after longer bleaching times. Initially, the consumption of oxygen is dependent upon the concentration of transition metal ion, but in less than 15 minutes these ions have no further influence on the reaction. Since major changes in the chemical and physical properties of the pulps occur during the first 15 minutes, the importance of the stabilization treatment cannot be too highly stressed. The consumption of oxygen can be represented as

$$-\frac{dO_2}{dt} \alpha\ [NaOH][O_2][M] \quad \text{during the initial stages}$$

$$-\frac{dO_2}{dt} \alpha\ [NaOH][O_2]^{\circ}[M]^{\circ} \quad \text{after prolonged reaction.}$$

Cotton cellulose reacted with oxygen under the bleaching conditions employed here in a completely different fashion than the pulps. Considerable induction occurred before the consumption of oxygen became appreciable. This behavior was also exhibited by a commercially bleached kraft pulp. From this behavior it was concluded that cellulose was degraded in a complex manner analogous but not identical to that already described in the literature for the aging of cellulose.

On the basis of these experiments and others involving pulps of varying lignin content, as well as on information derived and inferred from the literature,

it was hypothesized that the rapid oxidation of lignin-containing pulps is due to the greater production of peroxide intermediates capable of degrading cellulose. This peroxide is chiefly derived from the reaction of the lignin phenolic components with oxygen to yield degradation products and hydrogen peroxide. The degradation products can react further with oxygen and some (such as intermediate phenols and quinones) can produce addition peroxide when reacted with oxygen. The homolytic decomposition products of the peroxides (either produced spontaneously or through the intervention of certain transition metal ions) leads to cellulose degradation. It will be difficult, though not necessarily impossible, to separate the degradation of cellulose and lignin because they share a common highly degradative peroxide intermediate.

Examination of the physical and chemical properties of the pulps produced in this investigation showed most degradation occurred within 15 minutes of reaction and that the level of degradation was controlled chiefly by the initial caustic application. The greatest carbohydrate degradations (apart from those caused by metal catalysis) occurred initially at high lignin levels and eventually at very low lignin levels. Comparisons of carbohydrate degradation vs. delignification suggested high pressures of oxygen might be applicable at certain stages of the bleach to minimize degradation reactions.

Several methods for minimizing the peroxide degradation of pulp during oxygen bleaching processes were suggested for further testing. More effective application of stabilizers was demonstrated to be necessary whether or not other remedies were successful. The destruction of the peroxide precursors by reduction led to the stabilization of a pulp which had been oxidized with sodium chlorite but the reduction technique gave less outstanding results in the case of raw unbleached kraft pulp. These results demonstrated that the experiments described

by other researchers in which lignin was activated by an oxidative pretreatment before pulping or bleaching, or in which carbohydrate was to be stabilized to alkaline peeling by an oxidative technique before reaction with oxygen are doomed to failure unless a preliminary reduction is carried out.

The final experiments conducted in this project involve further investigations of chemical stabilization, the use of multistage oxygen bleaching to minimize pulp degradation and the comparative bleaching of these semibleached pulps with chlorine dioxide and hydrogen peroxide. The results of these experiments and the conclusions derived from them will be the subject of the next and final report.

FORWARD

Although oxygen bleaching was pioneered by Nikitin and Akim (1,2), the discovery by Robert and associates (3,4) of the protective action of $MgCO_3$ on the cellulosic portion of pulp finally made this process ready for commercial implementation. This discovery, at the present time, has led to the development of two oxygen bleaching systems. One group in South Africa, working in cooperation with Kamyr (Sweden), developed a process in which oxygen is used chiefly as a substitute for the chlorination stage (5). The other procedure which is used both in Sweden and the United States results from the cooperation of research groups at MoDoCell (Sweden) and Canadian Industries Ltd. (6). This process generally employs oxygen as one stage in a conventional bleaching sequence and cuts down on the chlorine requirements of all stages (7).

The present project, Project 3092, proposed that ultimately this development could be extended one step further and all chlorine-based chemicals might be eliminated from bleaching through the use of organic or inorganic peroxides, even ozone, in addition to the oxygen stage. Because of the great cost of the peroxides, it was decided at the July 27, 1972 meeting with the cooperators of this project that the initial studies be directed toward a better understanding of the potential of oxygen as a bleaching agent in order that the use of more esoteric chemicals might be minimized. The directions of this research were outlined in a previous memo (8) and preliminary work was discussed at a meeting in Appleton in March, 1973. This report covers the work accomplished to the end of June, 1973 and a further report will describe the final experiment.

INTRODUCTION

Oxygen bleaching may be conveniently thought of as consisting of two simultaneous general reactions, a desirable delignification reaction and an undesirable and closely related carbohydrate degradation reaction. This degradation reaction limits the acceptability of the oxygen bleaching process. It appears that a better understanding of these degradation reactions could lead to measures for the maximization of delignification relative to carbohydrate degradation. Since the project proposal was written, considerable additional information has become available in the literature. It is appropriate to review the major highlights in oxygen research applicable here.

One especially important advance was made by the Swedish researchers when they claimed the free radical mechanisms shown earlier to occur during the aging of the alkali cellulose at room temperature might also occur during the bleaching of pulp with oxygen at elevated temperatures (9,10). Several variations of these reactions have been proposed, but all were based upon the following scheme originally proposed by Entwhistle, et al. (11).

1. An initiation stage in which oxygen slowly reacts to form radicals

$$R_c\text{-CHO}^* + O_2 \longrightarrow R_c\text{-CO}\cdot + HO_2^\cdot$$

$$R_c\text{-CO}\cdot + O_2 \longrightarrow R_c\text{-CO (OO}\cdot)$$

$$R_c\text{-CO (OO}\cdot) + R_c\text{-H} \longrightarrow R_c\text{-CO (OOH)} + R_c^\cdot$$

2. A propagation stage

$$HO_2^\cdot + R_c\text{-H} \longrightarrow R_c^\cdot + H_2O_2$$

$$R_c^\cdot + O_2 \longrightarrow R_c\text{-OO}\cdot$$

$$R_c\text{-OO}\cdot + R_c\text{-H} \longrightarrow R_c\text{-OOH} + R_c^\cdot$$

*R_c = cellulose.

3. The stage in which contaminating transition metal ions catalyze cellulose degradation

$$R_c\text{-}OOH + M^{+2} \longrightarrow R_c\text{-}O\cdot + OH^- + M^{+3}$$

$$R_c\text{-}OOH + M^{+3} \longrightarrow R_c\text{-}OO + H^+ + M^{+2}$$

4. A termination stage which prevents the reaction from proceeding with explosive violence and which also results in the degradation of cellulose.

$$2\ R_c\text{-}OO\cdot \longrightarrow R_c\text{-}OH + R_c{=}O + O_2$$

At the time this scheme was originally presented, the effect of the hydrogen peroxide generated by the process was not known and degradation was related to the organic peroxide and transition metal ions only. Modern concepts claim that the homolytic decomposition of hydrogen peroxide provides additional $\cdot OH$ and $\cdot OH_2$ radicals, which under the more drastic conditions of the oxygen bleach (compared to viscose aging) attack cellulose in a manner similar to the organic radicals. The final termination stage provides a carbonyl group which, in the presence of alkali results in the cleavage of cellulose chains and in the destruction of many anhydroglucose units. These degradations are reflected in yield losses and in strength losses and will be described later in the introduction. The detection of unspecified peroxides (9,11), hydrogen peroxide (12) and certain organic acids (13) during oxygen bleaches together with harmful catalytic influences common to both suggests many similarities between oxygen and peroxide bleaching.

Many theories have been developed to relate the known beneficial effect of magnesium ion during oxygen bleaching with its similar effect during alkaline peroxide bleaching. Samuelson (9,12,14) and Croon suggested that magnesium ion complexes and stabilizes peroxides (15) thereby making them unavailable for

radical-redox reactions with transition metal ions. Experiments have shown that the transition metal ions are particularly harmful and catalyze cellulose degradation when they are present only in trace amounts. Others consider such stabilization unlikely (6,16) and suggest that the lower rates of degradation are the result of a deactivation of the transition metal ion by the magnesium ion itself. Robert (17) has suggested that the transition metal ions are absorbed on, or coprecipitated with an insoluble magnesium ion substrate, while Defaye and Godelle (18) believe the magnesium ion complexes with the reactive centers of the polysaccharide making it unreactive. Rapson and coworkers (19) studied the reaction of various cellulosic model substances with these reagents, as well as the stability of hydrogen peroxide with these reagents, and concluded that magnesium compounds deactivate transition metal ions by the formation of coordination compounds involving "oxo" or "hydroxo" bridges between them. These stable, not-readily-oxidizable complexes prevent the electron transfer reactions which promote cellulose degradation. Polarographic studies of the ferric ion-gluconic acid complex in alkaline solutions as well as ultraviolet studies indicate that interactions occur between magnesium ion and certain transition metal ions at definite molar ratios.

In a study of the degradation of methyl β-D-glucoside in an oxygen-alkali system, Sinkey (20) confirmed the formation of hydrogen peroxide as an intermediate in one of the degradative mechanisms of the glycoside and detected other more stable organic peroxides as well. He also confirmed Rapson's conclusion that magnesium ion interacts with the transition metal ions in some manner to prevent their action on hydrogen peroxide. A number of experiments comparing the effects of added peroxide, ferric ion, iodide ion and several complexing agents led him to the conclusion that trace metal ion-catalyzed

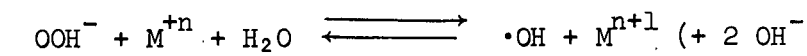
decomposition of the hydrogen peroxide by radical mechanisms leads to carbohydrate degradation. The reactions involved are the following:

1. Initiating reactions

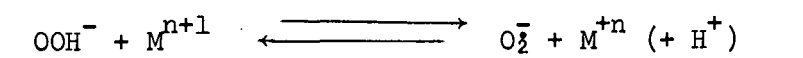
(1)

(2)

2. Catalytic effects

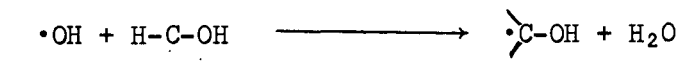


(3)

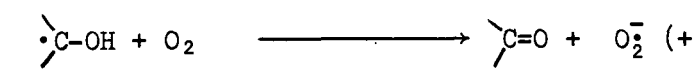


(4)

3. Degradation



(5)



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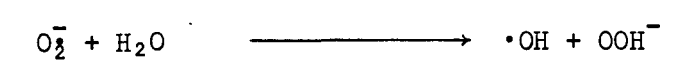
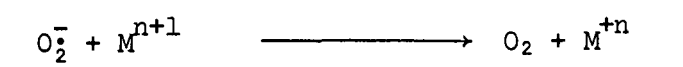
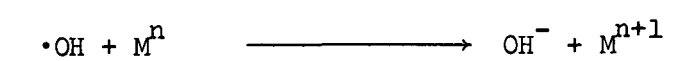


(7)

4. Termination



(8)



(9)

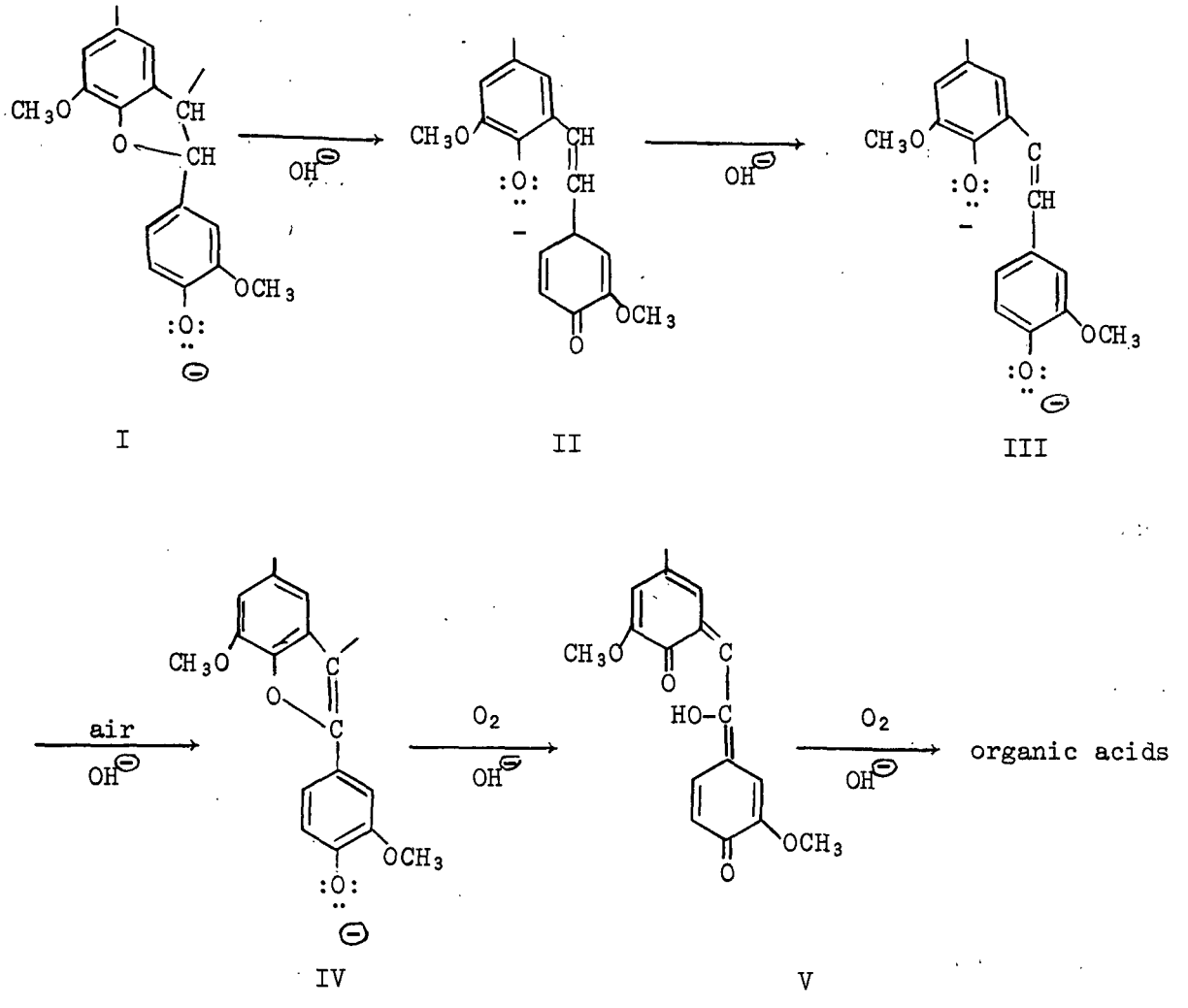
(10)

Many of the reactions shown above lead to the introduction of carbonyl groups into the cellulose molecule. Because of the alkalinity of the oxygen bleaching system, cleavage of the cellulose molecule and concomitant end-group "peeling" can occur and losses of both viscosity and pulp yield will result (21). In the case of methyl β-D-glucoside, the influence of the cleavage and peeling reactions are minimized and the kinetics of the reaction of the molecule with

oxygen and alkali may be studied. Sinkey (20) was able to analyze this system and show that after the induction period has ceased the degradation of the glycoside should be independent of the concentrations of peroxide and of transition metal ions. This was found to be true experimentally by Sinkey (20). Since magnesium ion reduces the effective transition metal content of the system, it too should not affect the ultimate steady-state rate of degradation of methyl β-D-glucoside. The presence of magnesium and transition metal ions exert their influences on the glycoside degradation only during the initial period of the reaction.

If these factors are also important during the bleaching of pulp with oxygen, the initial transition period between the onset of the bleach and the formation of appreciable quantities of hydrogen peroxide is the critical region in oxygen bleaching.

It is possible to speculate on the effect of lignin during oxygen bleaching on the basis of information available in the literature. Alkaline pulping delignifies wood by a series of reactions involving (among others) the cleavage of ether linkages and the liberation of phenolic groups of the lignin (22). Numerous reactions involving model substances, reviewed by Gierer (23) have demonstrated the likely major pathways involved in these reactions. For example, the reaction of a lignin grouping such as that shown below (I) with alkali yields a conjugated unsaturated quinoidal structure (II) which in turn rearranges to a conjugated phenolic structure (III). This potential quinone (III) is easily oxidized by oxygen to complicated conjugated phenolics (IV) and (V) (24). Because of the known relative ease of oxidation of most quinones (25), substance (V) will be easily oxidized by oxygen to a complex organic acid.



Thus, the potentially highly colored quinones (II) and (V) can be oxidized to colorless materials. The mechanisms by which these particular oxidations occur in lignin are not known although various pathways have been proposed (26).

This overall scheme constitutes a bleaching action, but indirect evidence in the literature suggests that one by-product from this bleaching action will be hydrogen peroxide. It is likely that oxidation of lignin phenols to quinones like the oxidation of other phenols (27) will produce hydrogen peroxide as a by-product. It has been demonstrated that the air oxidation of a leuco anthraquinone and anthraquinoid vat dyes sorbed onto cellulose fabrics produces hydrogen peroxide which

in turn oxidizes cellulose (27). In a like manner the oxidation of the lignin quinones [like the oxidation of other quinones (28)] will produce additional hydrogen peroxide which can oxidize the cellulose component of the pulp.

Thus, the extensive degradation of cellulose during oxygen bleaching appears to be due to free radical chain reactions initiated by oxygen whose rates are strongly influenced by the presence of hydrogen peroxide and transition metal ions. These factors, in turn, are dependent upon the existence of hydrogen peroxide precursors in the pulp itself which interact with oxygen and alkali to yield the harmful peroxide by-products. These precursors could include very reactive functional groups such as carbonyl groups common to both lignin and cellulose, less reactive functional groups such as alcohols which predominate in the cellulosic component of the pulp, or special chemical structures (most likely located in the lignin) which interact with oxygen to form hydrogen peroxide and additional hydrogen peroxide precursors. The complete elimination of cellulosic degradation during oxygen bleaching thus seems to be inherently impossible. However, there are good reasons for believing that the extent of degradation relative to delignification can be significantly decreased by minimizing the amount of peroxide formed from the lignin component.

EXPERIMENTAL

APPROACH

The investigation of oxygen bleaching reactions is quite complex. Many different reactions occur simultaneously, the reactions are sensitive to catalytic influences by contaminants or reaction products, and many oxidation products are more powerful than oxygen itself. Complications arise from the speed of formation and destruction of intermediates and the difficulty of attaining ideal experimental conditions (such as instantaneous penetration of chemical, isothermal reaction conditions and continuous measurement in change). For these reasons, most studies have avoided a kinetic approach, and have stressed the interpretation of the results of product analysis. With the exception of certain research conducted in the USSR (29), very little information on oxygen consumption kinetics has been published.

One of the guiding principles in this study has been the concept of competing rates of delignification and carbohydrate degradation. In this viewpoint, maximization of delignification with respect to carbohydrate degradation is essentially a kinetic problem. In order to obtain maximum information from a given experiment, it was felt to be necessary to be able to follow the course of the reaction as a function of time. It was recognized that it was not possible to follow the kinetics of all components (such as the alkali) involved in the reaction, but the kinetics of oxygen consumption did seem to be experimentally measurable on a continuous basis. Accordingly, data on oxygen consumption as a function of time were used to complement analyses of reaction end products and the extent of delignification and degradation.

The consumption of oxygen was followed by applying the ideal gas law to changes in pressure and temperature occurring within the reactor. The reactions were carried out under nearly isothermal conditions so that pressure changes were the main indication of oxygen consumption. A linear correction for temperature changes was applied. The volume of the reaction system was determined to permit the calculation of the number of moles of oxygen consumed. It was assumed that the perfect gas law applied and that oxygen was the only gaseous component involved in any changes. Analysis of gases from a reaction by mass spectroscopy showed the presence of small amounts of water vapor, hydrogen peroxide, carbon monoxide and traces of organic debris of uncertain origin. However, oxygen was the overwhelming component. Some of the temperature changes occurring in the gas during the initial stages of filling and initiating the reaction could not be followed with the reactor thermocouple. These were compensated for by means of a blank which was run with glass wool.

APPARATUS

The reaction system used in this study is shown in Fig. 1. The reaction vessel is a two liter, stainless steel, Parr bomb. The pulp is held in a removable teflon basket which fits snugly within the bomb. This prevented contact between the pulp and stainless steel vessel and any potential harmful catalytic influence. The cover to the bomb was modified to provide for oxygen and steam access, temperature measurement and a safety vent. All parts in contact with the pulp were teflon or teflon coated.

The system for introducing oxygen into the reactor also contained the means for measuring the pressure in the reactor. A Pace variable reluctance type differential pressure transducer was used to measure the pressure change

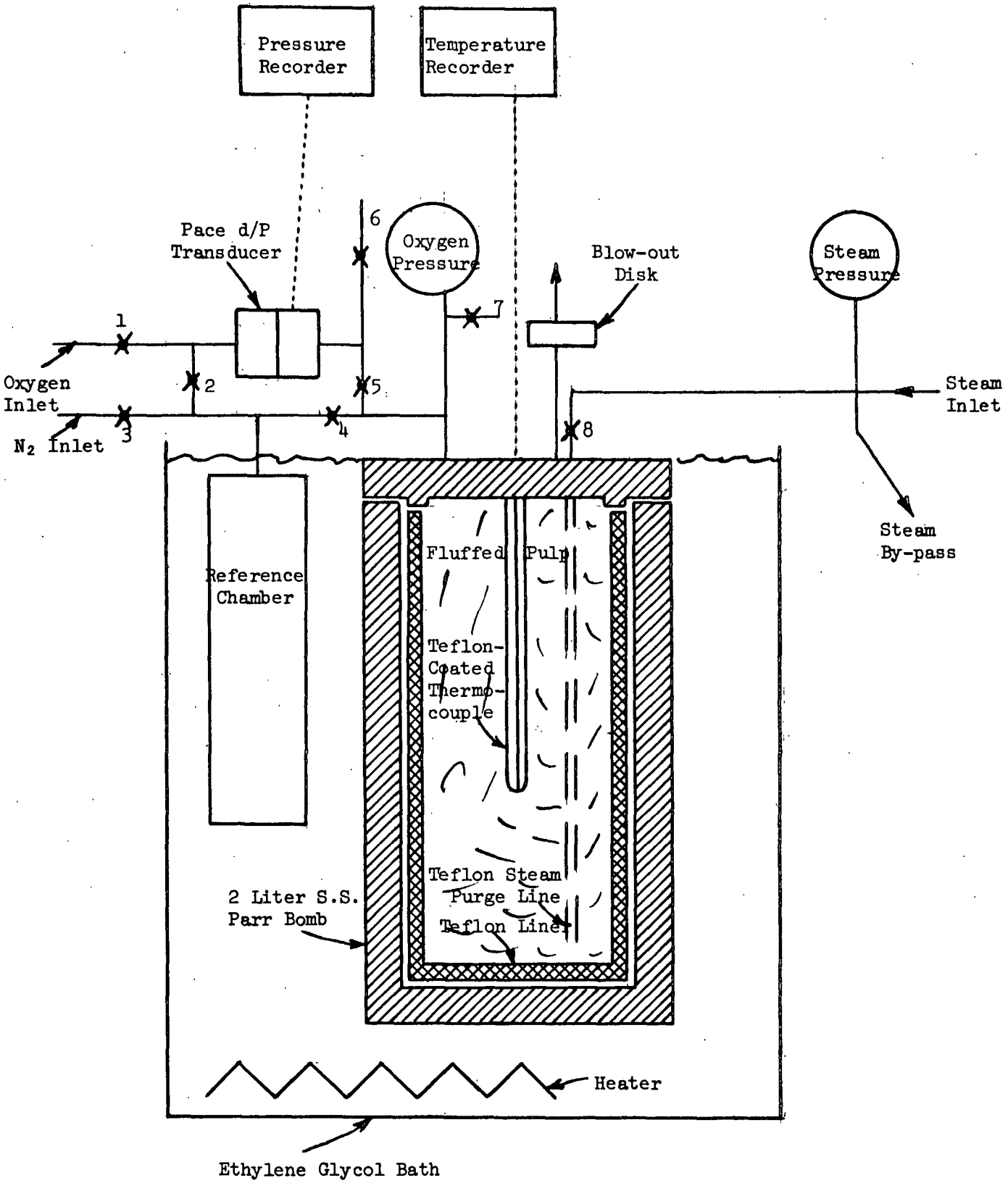


Figure 1. Schematic Diagram of Oxygen Bleaching Equipment

during the course of the reaction. One side of the Pace d/P cell was directly connected to the reaction vessel, while the other side was connected to a reference chamber maintained at the same bath temperature as the reaction vessel. When the system is first filled with oxygen, the valve [Valves 2 and 5 in Fig. 1] between the reference chamber and the reaction vessel is open and the pressure is the same in both vessels (differential pressure is zero). At the start of the reaction the valves are closed so that the reference chamber acts to store the initial pressure, and the d/P cell measures the change in pressure from the initial value. A Bourdon-type pressure gage is also connected to the O_2 supply to measure the absolute pressure level. A connection is provided so that N_2 can be used to flush the reactive gases from the system at the end of a run.

Low pressure steam was used to purge air from the system at the start of a run and to bring the pulp up to the 100°C. reaction temperature. Steam was introduced near the bottom of the reaction vessel through a teflon line, and vented from the line leading to the Bourdon gage. The steam was filtered to remove any condensate which might carry contaminant metals into the system.

The reaction vessel and reference chamber were submerged in an ethylene glycol constant temperature bath maintained at 100°C. ± 0.5°C. during the course of a run. It was possible to lower the hot bath and substitute a cold bath to quench the reactions at the end of a run.

Because of the sensitivity of the differential pressure to small changes in temperature between the reference chamber and the reaction vessel, the temperature of these components was carefully monitored and the apparatus was shielded to eliminate drafts. For study of short duration reactions (less than 15 minutes) oxygen preheated to 100°C. was used.

PROCEDURES

Most of the pulp used in this investigation was an unbleached kraft pulp supplied by Champion International. The pulp was received at 12% consistency, diluted to 2% consistency, acidified to pH 3 with sulfuric acid, washed with water until the pH had increased to that of the water supply, centrifuged to 30% consistency, bagged and refrigerated.

The pulp charge used for a bleaching experiment contained 120 g. on an o.d. basis. It was soaked in an alkaline solution for 30 minutes and filtered to a total weight of 400 grams. The charge of alkali was empirically determined to leave either 6.6, 3.3, or 1.7% alkali on the pulp after this treatment. The pulp pad was then fluffed mechanically while $MgCO_3$ stabilizer (usually 1% of the pulp) was added. The fluffed pulp was placed in the teflon container and placed in the reactor.

The reaction chamber and baths were first brought to 100°C. Four steam purges were then used to remove air and bring the pulp to temperature. The oxygen was then rapidly introduced into the pressure chamber and the ΔP measurement begun. Upon completion of the bleach, the cooling bath was substituted for the heating bath and the oxygen was flushed from the reactor with nitrogen. The pulp was suspended in 4 liters of water (the filtrate of this stage was saved) and the pulp washed until the effluent was clear and no longer alkaline.

ANALYSIS

In addition to the temperature and pressure measurements mentioned earlier which monitored the progress of the bleach, the quality of the pulp and the composition of waste liquors were also measured. Some tests such as the

content of organic material in the waste liquor were discontinued when it was found to correlate well with the inverse of the simpler and more useful yield measurement. In the case of the pulp analyses, some tests originally chosen were abandoned after initial trials when no significant information was obtained and other tests such as carbonyl were initiated when their value became apparent at a later date.

The chemical properties of most value were yield, viscosity (TAPPI T 230 su-66), alpha or gamma cellulose (TAPPI T 225 m-60), and brightness and brightness reversions (TAPPI T 452 m-58). The permanganate number (TAPPI T 214 su-71) was chosen over the more popular Kappa number (TAPPI T 236 m-60) because of the smaller sample size required. An empirical relationship between the permanganate number used here and the Kappa number was determined in the range of interest.

The paper evaluation tests carried out on unbeaten pulp included zero-span tensile, M.I.T. fold, tear factor, and burst factor. With the exception of the zero-span test, these values have little significance since no beating evaluations were carried out. It was hoped that very poor properties would be indicative that significant degradation has occurred.

RESULTS

INTRODUCTION

Although the oxygen pressure and the temperature of the reactor were measured continuously during the bleach, the changes in the properties of the pulps and in composition of the bleaching liquors could not be obtained as easily. Where changes in pulp property with time was desired, separate bleaches were carried out for 15, 30, 60, and 120 minutes. Since the pressures and the temperatures were continuously recorded during all these repetitive bleaches, considerable replication existed at the shorter bleaching intervals. Some bleaches were carried out for 120 minutes for consumption studies and only single or occasionally duplicate runs were available for kinetic analysis in those instances. An average curve was drawn through the points and the values at 5-minute intervals were corrected by subtracting the glass wool blank described earlier. Since a significant heat of reaction was always obtained during bleaching, the resulting change in pressure had to be corrected for temperature changes. This correction, together with the conversion of the data to grams of oxygen consumed per 100 grams of pulp being bleached, is given by the following expression:

$$\text{g. } O_2/100 \text{ g. pulp} = 3200/\text{g. o.d. pulp}\left(\frac{V_o - \frac{\text{g. o.d. pulp}}{154\ 0} - \frac{\text{g. } H_2O}{1000}}{373\ R}\right)\left(\Delta P + P_o \frac{T_2-100}{373}\right) \tag{11}$$

$$= 0.0971\ (\Delta P + 144.7\ (\frac{T_2-100}{373})) \tag{12}$$

where

R = gas constant $\left(\frac{\text{liter, p.s.i.}}{\text{g. mole, } ^\circ\text{K.}}\right)$

ΔP = apparent loss of oxygen pressure

P_o = pressure employed during the bleach

T_2 = heat of reaction within the reactor

V_o = total volume of reactor corrected for probes and container.

Consumption data for an unbleached kraft which contained only traces of transition metal ion and which was bleached at three levels of alkali on pulp 6.6, 3.3, and 1.7% are shown in Fig. 2. Curves of this type can be used not only to show the consumption of oxygen at any time up to 120 minutes, but also to measure the rate of oxygen consumption by drawing the tangent to the curve at the particular time in question. No simple kinetic interpretation of these curves can be made since the order with respect to time is not constant. This behavior is also typical of the kinetic behavior of various glycosides when reacted with oxygen in alkaline solution and reflects the many catalytic and poisoning influences which occur in these reactions (20,32).

The two different types of pulp employed in this investigation were cotton linters and a commercial southern pine kraft pulp supplied by Champion International Paper Co. The latter pulp was modified in several ways in an attempt to study the effect of various parameters such as changes in the content and nature of lignin, transition metal ion content, and the effect of fiber structure. The pulps employed for these purposes are listed in Table I. In the text the individual bleaches of pulps from these series are given a second letter designation in order to facilitate identification.

It is possible to determine the influence of different parameters upon the oxygen bleaching reaction by determining the initial reaction rate before the catalytic and poisoning effects manifest themselves (33). By varying the concentration of significant parameters and measuring their influence upon the initial rate of oxygen consumption a kinetic interpretation of a complex system is possible. The parameters varied in this investigation were alkali and transition metal ion concentration, oxygen pressure, and lignin content. By substituting the appropriate values in the following expression:

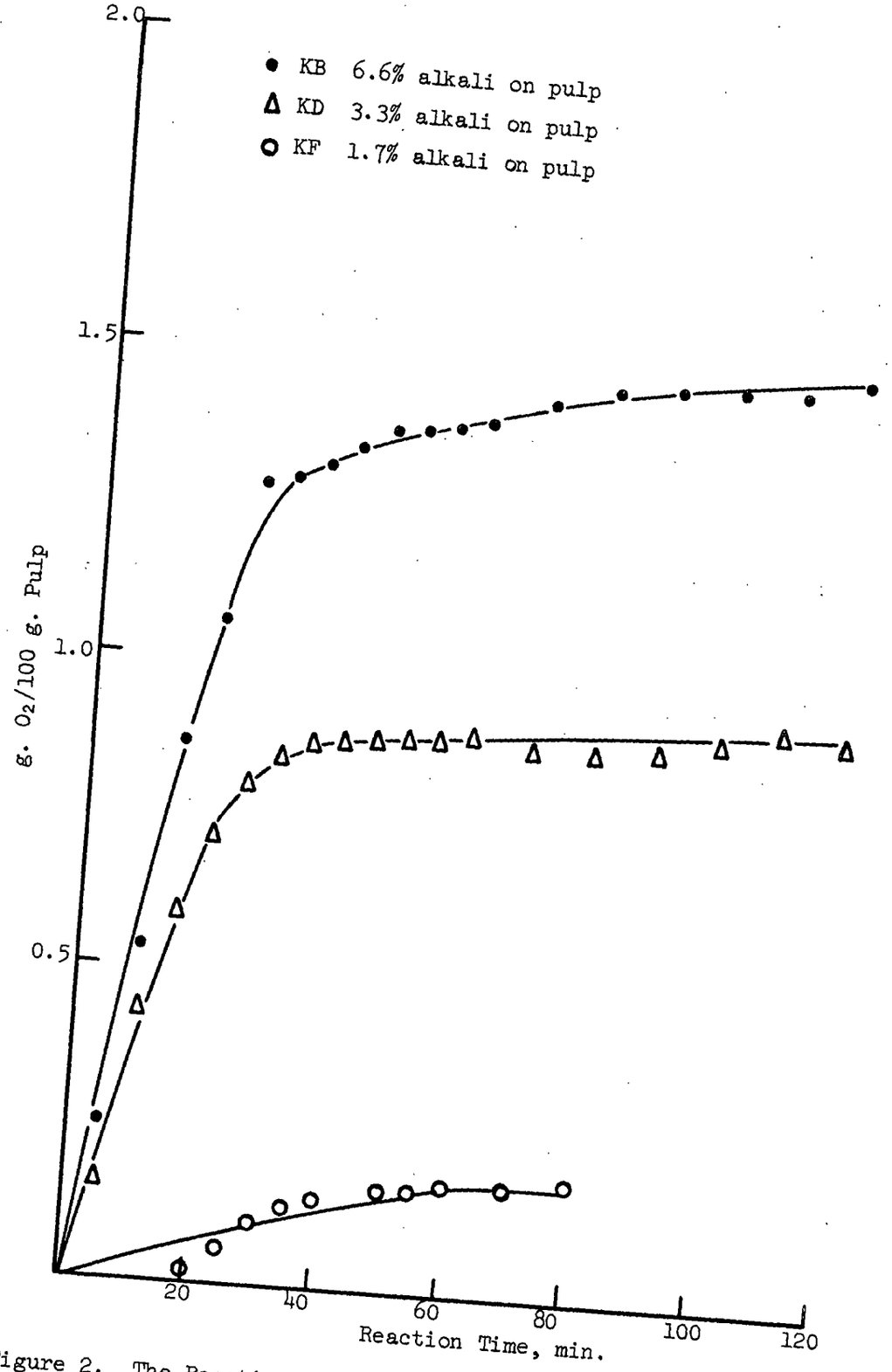


Figure 2. The Reaction of Unbleached Kraft Pulp (Series K) with 130 p.s.i.g. Oxygen at 100°C. and Different Alkali-to-Pulp Ratios

$$\log [dP/dt]_i = A + n. \log [X]_i \qquad (13)$$

their influence upon the consumption of oxygen may be given a quantitative form. The quantity $[dP/dt]$ is the initial rate of oxygen consumption, X is the concentration of the parameter under investigation, A is a constant, and n is the order of the reaction.

TABLE I

PULPS EMPLOYED FOR THE STUDY OF OXYGEN BLEACHING

Pulp Series	D	E	F	G	H	J	K	M
Southern pine kraft (Champion Papers)	+	+	-	+	+	+	+	+
Cotton linters PS-57 (Hercules)	-	-	+	-	-	-	-	-
High transition metal ion content	+	-	-	-	-	-	-	-
Medium transition metal ion content	-		-	+	+	+	-	+
Low transition metal ion content	-	+	+	-	-	-	+	-
Chlorited	-	-	-	+	+	+	-	-
Commercially bleached	-	+	-	-	-	-	-	-

PULPS WITH LOW TRANSITION METAL ION CONTENT

Effect of Alkali

The pulp chosen for this investigation (the K-series of pulp) contained only 82 p.p.m. total transition metal ion (the sum of the contents of V, Ti, Fe, and Cu) as determined by flame spectroscopy. This is in the range of composition typical of pulps supplied for commercial oxygen bleaching in South Africa (31). A set of curves describing the consumption of oxygen by this pulp at 6.6, 3.3, and 1.7% alkali on the pulp at 100°C. and 130 p.s.i.g. oxygen is shown in Fig. 2.

Two of the curves for these bleaches showed a rapid initial consumption of oxygen followed by a marked slowing of the consumption. The very small consumption curve for the pulp reacted with 1.7% alkali contained relatively large experimental errors. For this reason, the indicated induction period which occurs before significant oxygen consumption is thought to be an artifact.

The change in pH which occurs during the bleaches at different times is shown in Table II and indicates that most of the alkali is consumed in less than 15 minutes. Salts of carbonic acid and various organic acids are produced. This rapid consumption of alkali in the case of pulps bleached at lower alkalinities might delay the formation of necessary intermediate compounds capable of furthering oxidation, thus leading to the appearance of induction periods. This conjectured intermediate may well be the hydrogen peroxide by-product shown to have a significant effect upon the degradation of polysaccharides by others.

TABLE II

CHANGES IN THE pH OF THE BLEACHING LIQUOR DURING THE BLEACHING OF KRAFT PULP[a]

Time of Reaction, min.	Initial Percent of Alkali on Pulp		
	6.6	3.3	1.7
0 (before heating to temp.), pH	∿14	∿14	∿14
0 (after heating to temp.), pH	12.1	11.7	10.9
5, pH	11.9	--	--
15, pH	11.7	--	--
30, pH	11.2	--	--
60, pH	10.7	--	--
120, pH	9.9	9.4	8.4

[a]Reacted with 130 p.s.i. oxygen at 100°C. and 25% consistency.

From the consumption curves shown in Fig. 2, it is possible to measure graphically the rate of oxygen consumption at 0, 15, and 30-minute time intervals. A plot of the logarithm of the reaction rates at different times up to 60 minutes reaction against the logarithm of the hydroxyl ion concentration in the case of bleaches at 6.6% alkali on the pulp indicates an apparent order of 0.8. This value was considered to indicate an apparent first-order dependence of oxygen consumption on the alkali content. Unfortunately, data were not available to make the corresponding calculations of the apparent order for the bleaches conducted at the other alkali-to-pulp ratios. If the abnormal curve of bleach KF is ignored, bleaches KB, KU, and KD (see Table III) indicate that the initial consumption of oxygen has an apparent first-order dependence upon the initial applied alkali at the 15 and 30-minute time intervals! This phenomenon is typical of the kinetic behavior of all the bleaches studied here where the alkalinity of the system is varied. It is possible that this behavior reflects the rapid formation of an intermediate whose concentration is proportional to the applied alkali. This intermediate would be oxidized by oxygen and replaced in part with other intermediates capable of reacting in a similar manner. The hydroxide ion content would be consumed as acidic products were formed. Thus, the consumption of the oxygen at different time intervals could be seemingly dependent upon the concentration of the initial applied alkali as well as on the subsequent alkalinity changes. This intermediate could be an enolate or phenolate derivative of lignin whose existence would be unaffected by liquor pH values greater than 11. After prolonged oxidation when the liquor pH becomes substantially less than this value, or when the concentration of the conjectured intermediate becomes negligible, any subsequent consumption of oxygen (if any) will be independent of even the initially applied alkali.

TABLE III

CHANGES IN THE RATE OF CONSUMPTION OF OXYGEN BY KRAFT PULP WITH TIME AND ALKALINITY[a]

Sample	KB	KU	KD	KF[a]	Apparent Order[b]
Alkali on pulp, %	6.4	4.9	3.3	1.7	--
$MgCO_3$ on pulp, %	1	1	1	1	--
Initial rate, g. O_2/100 g. pulp/min.	0.0710	0.0610	0.0588	0.0050	0.5
15-Min. rate, g. O_2/100 g. pulp/min.	0.0455	0.0318	0.0258	0.0045	0.7
30-Min. rate, g. O_2/100 g. pulp/min.	0.0107	0.0100	0.0051	very small	0.9
Total consumption after 120 min. reaction, g. O_2/100 g. pulp	1.50	1.18	0.92	0.20	--

[a]These data were not used in the calculation of apparent order.

[b]The order at the different time intervals was determined by plotting the rate of oxygen consumption at a given time against the initial alkali in Equation (13).

It is likely that such an intermediate would be oxidized to a variety of organic products and peroxides. Because of the rapid decomposition of the peroxides under the conditions of oxygen bleaching (20), they must be continually replaced from certain of the unreacted intermediates, or precursors. These peroxidic products and their radical decomposition products are thought to be more powerful oxidants than oxygen itself (28). Many of their oxidation products must be capable of consuming additional oxygen in order to account for the great consumption of oxygen recorded in Fig. 3. Because of this complex situation, it is not correct to equate the consumption of oxygen with the degradation of the pulp.

Ultimately, a condition is reached where the pH diminishes to some undetermined value less than 11, the major peroxide precursors are reduced to a minimum and the oxidizable enolate and phenolate ions are either destroyed or exist chiefly in the slowly reacting hydroxide form. The rate of consumption of oxygen then approaches zero order as far as the effect of many external variables is concerned and has no bleaching significance.

Effect of Bleaching Time

The changes in the chemical and physical properties with time of the K-series of pulps (low in transition metal ion content) bleached at 100°C. and 130 p.s.i.g. oxygen were also measured at reaction times of 15, 30, 60, and 120 minutes. The chemical tests included measurements of yield, lignin, viscosity, and brightness. The physical tests were more limited because the small size of the bleached pulp sample (about 100 g.) did not permit a beater evaluation and because samples were needed for subsequent comparative bleaching. The tests thought to be of some significance were zero-span tensile, M.I.T. fold, and the tear and burst factors.

The changes in both the chemical and physical properties of the K-series pulps with time when reacted with oxygen at 6.6% initial alkali concentration based on the pulp are shown in Table IV. The results demonstrate that the chemical properties of the pulps are determined within the first 15 minutes of reaction and, that, apart from a continuous brightness increase, little additional change occurs in the other properties. In this first interval the viscosity of the pulp is halved and this observation is in agreement with published technological experience (31). The increase in pulp brightness on aging for 1 hour at 105°C. is contrary to most brightness experience and may be rationalized by conjecturing that peroxides analogous to the stable organic peroxides observed

by Sinkey may be present on the cellulose. The pyrolytic decomposition of these relatively stable peroxides during heat aging may generate hydrogen peroxide which in turn can cause additional bleaching. It is not known whether this behavior will also occur on storage or whether, if it does occur, if it will be detrimental to pulp quality after such aging.

TABLE IV

CHANGES IN THE CHEMICAL AND PHYSICAL PROPERTIES OF SOUTHERN PINE KRAFT PULPS BLEACHED AT 100°C. AND 6.6% CONSISTENCY CAUSTIC WITH 130 P.S.I. OXYGEN FOR DIFFERENT TIMES

Sample	KE	KG	KA	KB	Unbleached
Time, min.	15	30	60	120	--
Oxygen consumed, g. O_2/100 g. sample	0.65	1.26	1.40	1.50	--
Yield, %	95.4	95.5	94.4	93.4	--
Viscosity, cp.	15.3	14.6	14.4	13.5	30.5
K-number	7.6	8.1	6.2	6.1	20.1
α-cellulose, %	86.9	86.7	86.6	96.7	92.0
Brightness	36.4	39.4	43.0	45.4	22.7
Brightness reversion	37.2	40.3	43.5	45.8	22.6
Zero-span tensile, km.	13.4	13.9	13.3	13.6	--
M.I.T. fold	33	21	23	25	--
Tear factor	243	238	238	226	--
Burst factor	20.7	20.7	20.7	21.7	--

The physical and chemical properties of the pulps bleached for 120 minutes at 100°C., 130 p.s.i. oxygen pressure and at 6.6, 3.3, and 1.7% sodium hydroxide concentrations are given in Table V. In all cases, the chemical properties changed to a value determined by the initial caustic concentration

in a manner similar to the behavior of the bleach at 6.6% alkali described above (see Appendix). The changes in the physical properties were less dramatic but also reflected the predominating influence of the initial alkali concentration and is also in agreement with that reported by the commercial installation in South Africa (18).

TABLE V

CHANGES IN CHEMICAL AND PHYSICAL PROPERTIES OF SOUTHERN PINE KRAFT PULPS WITH INITIAL ALKALINITY BLEACHED AT 100°C., 130 P.S.I. OXYGEN FOR 120 MINUTES

	KB	KD	KF
Alkalinity, %	6.4	3.3	1.7
Oxygen consumed, g. O_2/100 g. sample	1.50	0.92	0.20
Yield, %	93.4	100	99.5
Viscosity, cp.	13.5	17.0	22.2
K-number	6.1	8.1	13.8
α-cellulose, %	80.7	86.9	89.0
Brightness	45.4	38.0	28.6
Brightness reversion	45.8	38.3	29.2
Zero-span tensile, km.	13.6	14.8	14.7
M.I.T. fold	25	38	27
Tear factor	22.6	24.3	28.0
Burst factor	21.6	24.2	20.8

Effect of Oxygen Pressure

The dependence of the rate of oxygen consumption on the pressure of the applied oxygen was also determined by bleaching the series K pulp (low in transition metal ion) with oxygen at 65, 97.5, 130, and 195 p.s.i. for 120 minutes at 100°C. and 6.6% alkali with the conventional 1% of magnesium carbonate added.

The consumption of oxygen which occurred during these bleaches is shown in Table VI and Fig. 3. There is no indication of an induction period since the alkali contents were high enough to ensure the formation of appreciable quantities of the conjectured enolate and phenolate derivatives of the lignin. In the case of bleach KF, the hydroxyl ion content was too low for the formation of large quantities of intermediates. In the case of the other bleaches, the pH of the bleaching liquor had not decreased to a low enough value to convert these ions to the respective less easily oxidized hydroxy compounds until after 30 to 60 minutes reaction had occurred.

TABLE VI

THE RATE OF OXYGEN CONSUMPTION OF SOUTHERN PINE KRAFT PULPS BLEACHED AT 100°C., 120 MINUTES, AT 6.6% ALKALINITY AND AT 195, 130, 97.5, AND 65 P.S.I. OXYGEN

	KP	KB	KQ	KR	Order with Respect to Applied O_2	Order with Respect to Actual O_2
Applied oxygen pressure, p.s.i.g.	195.0	130.0	97.5	65.0	--	--
Initial rate, g. O_2/ 100 g. pulp/min.	0.0700	0.0710	0.0595	0.0417	0.7	0.7
15-Min. rate, g. O_2/ 100 g. pulp/min.	0.0330	0.0455	0.0265	0.0235	1.0	1.2
30-Min. rate, g. O_2/ 100 g. pulp/min.	0.0150	0.0097	0.0155	0.0123	0	0
Total consumption, g. O_2/100 g. pulp at 120 min.	1.58	1.50	1.18	1.13	--	--

The data in Table VI indicate that the pulp consumes oxygen at a rate having a first-order dependence on oxygen pressure when the pressure is less than 195 p.s.i.g. The shape of the consumption curve at that pressure is real and indicates some change in mechanism must have occurred. Although

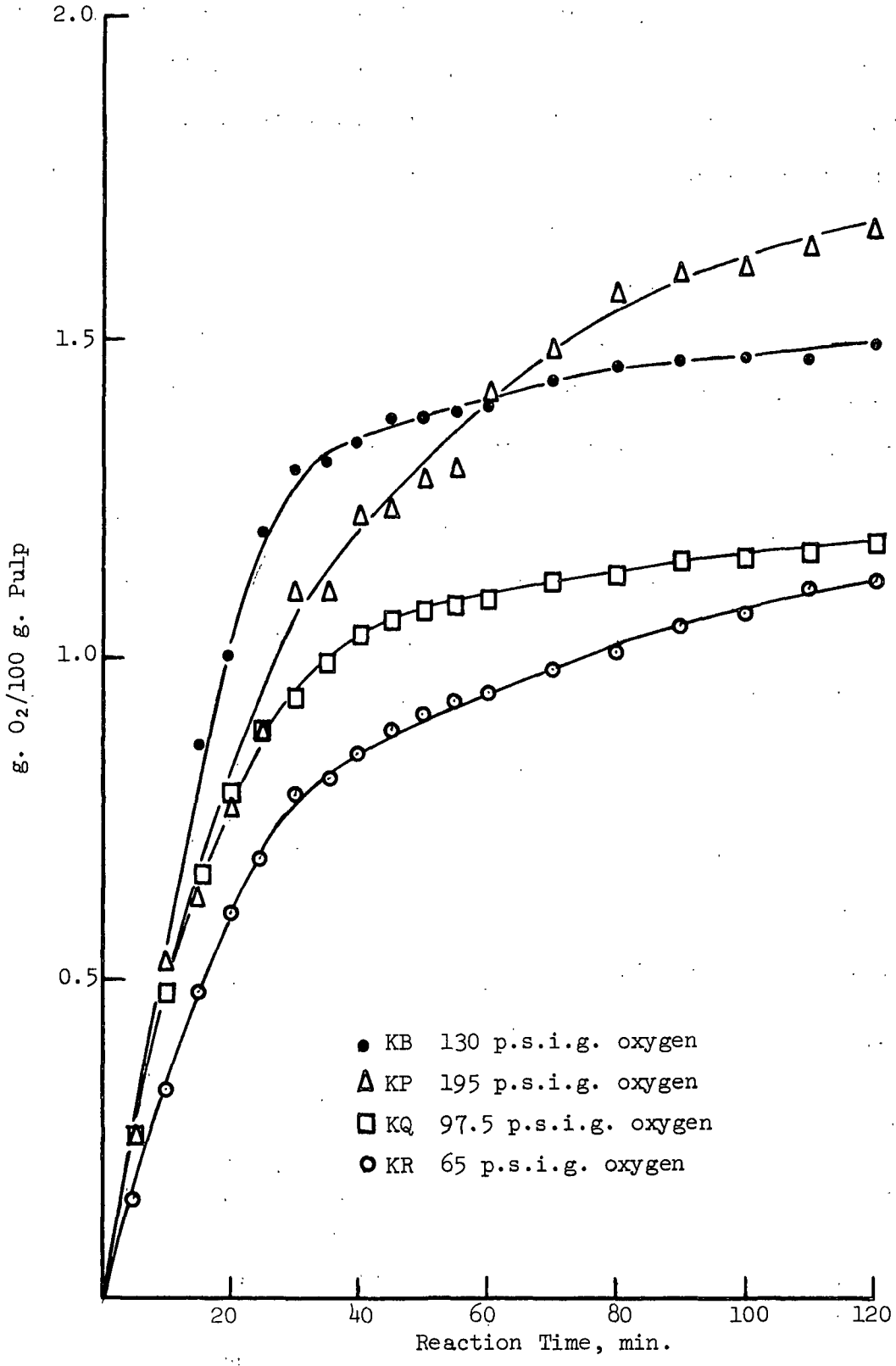


Figure 3. The Reaction of Unbleached Southern Pine Kraft Pulp (Series K) with 6.6% Alkali on Wood, 100°C. and Varying Oxygen Pressure

many are possible, the most likely involves the control of the reaction by the availability of reaction sites when the quantity of oxygen available for reaction is great enough. This speculation is favored because of its consistency with other results to be discussed later. Prolonged oxidation beyond 15 minutes results in the eventual destruction of most oxidizable centers in the pulp and results in a reaction in which the slow continuous consumption of oxygen gas is not dependent on the oxygen pressure. This behavior may be the result of either the loss of easily oxidized material due to the depletion of the hydroxyl ion and/or to the poisoning effects noted in some model experiments (32).

The changes in the chemical and physical properties of the pulps as a result of changing the oxygen pressure are shown in Table VII. Some experimental uncertainty is present, nevertheless brightness and delignification are increased by increasing the pressure while the pulp viscosity and the yields are decreased.

TABLE VII

PROPERTIES OF SOUTHERN PINE KRAFT PULPS BLEACHED AT 100°C., 120 MINUTES, 6.6% ALKALI AND OXYGEN PRESSURE

	KP	KB	KQ	KR
Applied oxygen pressure, p.s.i.g.	195	130	97.5	65
Yield, %	92.1	93.4	91.8	93.7
Viscosity, cp.	12.5	13.6	14.1	13.0
K-number	5.9	6.6	7.0	6.9
α-cellulose, %	87.0	86.7	86.9	88.1
Brightness	47.6	45.8	43.3	41.8
Brightness reversion	48.1	45.8	43.7	42.9
Zero-span tensile, km.	13.2	13.6	13.7	14.2
M.I.T. fold	38.0	25.0	42	41
Tear factor	247.0	226.0	242.0	229
Burst factor	22.9	21.6	22.2	23.6

On the basis of this work, it can be concluded that the experimental procedures employed here yield results that where an overlap occurs are comparable to those reported by others using different techniques (18). The properties of the pulps are changed very rapidly during bleaching to a value determined principally by the applied alkali. The bleaching action, on the other hand, does not occur as rapidly as delignification. Viscosity loss progresses at a rate dependent upon the time of reaction as well as on the other experimental conditions such as alkali content.

The rate of consumption of oxygen during the bleach shows that the reaction is very complex but that it may be divided into at least two phases which may have both practical and theoretical significance. The first of these is an initial phase in which many uncertainties such as the solution and the penetration of oxygen exist, where the formation of reactive intermediate substances such as enolates and phenolates occurs, and where these ionic substances react with oxygen to form hydrogen peroxide and additional peroxide precursors. In this region, most of the chemical and physical transformations the pulp undergoes will occur. These transformations include loss of lignin, of viscosity, and paper properties but not the major change in brightness. The final stage occurs when the consumption of oxygen and the change in the chemical and physical properties of the pulp approach zero-order dependence on the external variables.

When little transition metal ion is present, and its effect is overcome by the magnesium ion stabilizer, the following generalities were obtained:

$$\frac{-dO_2}{dt} = [NaOH]^{1*} \cdot [O_2]^1 \quad \text{during the initial stages} \qquad (14)$$

*The concentration of caustic can be the initial applied alkali on pulp as well as the actual concentration.

After 15 minutes reaction, the following generalization seems to be true:

$$\frac{-dO_2}{dt} = [NaOH]^{1*} \cdot [O_2]^{o} \qquad (15)$$

THE EFFECT OF TRANSITION METAL IONS ON PULP BEHAVIOR DURING OXYGEN BLEACHING

Pulp Composition

Since the effect of metal ion contamination is of interest (and often unavoidable in practice) the copper content of the pulps was taken as a variable in these experiments. On the basis of limited evidence in the literature (19,30), it is assumed that other transition metal ions such as iron and cobalt will show a behavior similar to copper. The metal contamination encountered here will differ from the contamination associated with the treatment waters and the techniques for countering those effects could differ significantly. The trace metal contents of the unbleached pulps used in the present report are listed in Table VIII. The washing treatments employed here did reduce the calcium, barium, sodium, aluminum, and silicon contents but produced questionable changes in the magnesium, boron, and titanium contents and actually increased the copper and iron contents of the pulps. The total transition metal ion content of the pulps studied here was taken to be the sum in parts per million of copper, iron, titanium, and vanadium ions. The compositions of the original pulp and of pulp Series K was within the range of values obtained by S.A.P.P.I. in South Africa (30) over a long period of time.

*The concentration of caustic can be the initial applied alkali on pulp as well as the actual concentration.

TABLE VIII

THE METAL CONTENT OF UNBLEACHED SOUTHERN PINE PULPS

	Original Pulp	K-Series	M-Series	D-Series
Total ash	0.95	0.60	--	0.55
Ba, p.p.m.	18	2.2	2.2	1.7
Ca	2400	1700	1446	1500
Mg	660	670	464	440
Sr	--	--	12	--
Na	1000	68	115	85
B	0.8	--	0.3	0.3
Al	130	58	20	64
Si	560	220	293	300
Pb	1.3	1.2	8.8	6.0
Cu	1.1	3.6	102	200
Fe	48	70	19	46
Ti	20	7.7	4.4	5.4
V	1.7	0.6	1.8	1.0

Effect of Transition Metal Ions

Pulps at these three levels of transition metal ion content (Series K, M, and D) were bleached under identical conditions using 130 p.s.i. oxygen pressure, 100°C., for 120 minutes at 6.6% added alkali. Magnesium carbonate (1% on pulp) was added during the fluffing stage in the conventional manner. The consumption of oxygen was followed as before and no induction period was observed. Very large differences in the heat of reaction were observed, the temperature of the pulp in bleach KB rose to 108.5°C. in 15 minutes, that of bleach MA rose to 117.5°C. in 20 minutes, while the temperature of bleach DH rose to 121.5°C. in 15 minutes. The temperatures inside the reactors then decreased over a 30-minute period to the bath temperature (100°C.).

Pulps MA and DH which had higher transition metal ion contents reacted more quickly, were more exothermic and ultimately consumed more oxygen than the pulp (KB) with a lower ion content. These data are given in Table IX and illustrate the profound effect of transition metal ion on the consumption of oxygen during bleaching. Initially, the consumption of oxygen is directly dependent upon the concentration of the total transition ion content of the pulp but the apparent order of the reaction decreases from this initial value of unity to zero order. The oxidation reaction after 30 minutes proceeds at a rate that is independent of the concentration of these metal ions. This behavior has also been shown to exist in the case of the degradation of methyl β-D-glucoside in alkaline solution by Sinkey (23). Although it is possible that the loss of alkalinity is responsible for the decreasing importance of the transition metal ion, the effect of the interaction of kinetic variables shown by Sinkey (20) to be responsible for similar behavior in model systems is the explanation favored here. It has been postulated (23,30) that these ions catalyze the decomposition of the by-product hydrogen peroxide by a free radical mechanism. These radicals in turn promote the degradation of polysaccharide material. The elimination of these radicals by causing the peroxide to decompose by an ionic mechanism will stop this type of polysaccharide degradation. Magnesium ion was thought to interfere with the ability of the transition metal ion to catalyze the radical decomposition of the peroxide which can then presumably decompose by both radical and ionic mechanisms.

Because of the lack of induction periods, the initial reaction with oxygen must be fast and hydrogen peroxide must be formed very rapidly. The products of the hydrogen peroxide degradation of both lignin and polysaccharide must then react very rapidly with additional oxygen. If this is true, the rapid

initial reaction is not hindered by the transport of oxygen from the gas phase to the reaction sites. The initial first-order dependence on transition ion concentration is consistent with the ideas proposed by Sinkey (20) and not with the initiator concept as proposed for other systems in the literature (33). On the other hand, it is still uncertain whether the metal ions can contribute in this relatively simple way to the oxygen consumption or whether they can also contribute to the reaction by hydroxylating aromatic rings [as they do in certain model studies (34)], thus forming more phenolic substances which in turn contribute to the production of additional hydrogen peroxide.

TABLE IX

THE EFFECT OF TRANSITION METAL IONS ON THE RATE OF OXYGEN CONSUMPTION OF SOUTHERN PINE KRAFT PULPS[a]

	DH	MA	KB	Apparent Order
Transition metal ion content, p.p.m.	252	127	82	--
$MgCO_3$ on pulp, %	1	1	1	--
Initial rate, g. O_2/100 g. pulp/min.	0.192	0.125	0.0710	1
15-Min. rate, g. O_2/100 g. pulp/min.	0.0335	0.0345	0.0455	0
30-Min. rate, g. O_2/100 g. pulp/min.	0.0086	0.0080	0.0097	0
Total consumption after 120 min. reaction, g. O_2/100 g. pulp	2.00	1.66	1.50	--

[a]The pulps were reacted with 130 p.s.i. oxygen, 100°C., 6.6% consistency for 120 minutes.

The physical and chemical properties of the pulps bleached in the presence of varying quantities of transition metal ions are given in Table X. The pulp yield, α-cellulose content, viscosity and papermaking properties are all greater when the transition metal ion concentration is diminished. The

great sensitivity of these properties to metal ions serves to emphasize the need to eliminate them as completely as possible from the oxygen bleaching system. These contaminants can be brought in with the pulp itself, the processing water or can be introduced from equipment. In these experiments, a constant amount of magnesium carbonate was always added before bleaching. Although this quantity is in excess of the amounts claimed by Rapson as necessary to inhibit the actions of iron and copper (19), it may be that the magnesium ion must dissolve and penetrate the fiber wall to finally interact with the metal. The effectiveness of the magnesium was obviously poor since the treated pulps did not have properties approaching those of the pulp containing less of the transition metal ions.

TABLE X

THE EFFECT OF TRANSITION METAL IONS ON THE PROPERTIES OF SOUTHERN PINE KRAFT PULPS AFTER OXYGEN BLEACHING[a]

	DH	MA	KB
Total transition metal ion content, p.p.m.	252	127	82
Yield, %	88.6	91.7	93.4
Viscosity, cp.	4.8	6.4	13.4
α-Cellulose, %	82.6	84.2	86.7
K-number	6.2	5.3	6.6
Brightness	42.6	48.7	45.4
Brightness reversion	43.0	49.1	48.8
Zero-span tensile, km.	8.8	10.2	13.6
M.I.T. fold	6	22	25
Tear factor	56.8	110	136
Burst factor	18.9	25.8	21.8

[a]The pulps were bleached with 130 p.s.i. oxygen, 100°C., 6.6% alkalinity for 120 minutes.

Effect of Alkali

Because of this pronounced effect of the transition metal ion on the rate of consumption of oxygen during the bleach, the effect of these ions in conjunction with other parameters such as alkalinity and oxygen pressure was also studied. The effect of alkalinity is shown in Table XI. Like the behavior of the K-series of pulps (low in transition metal ions), these bleaches showed no indication of an induction period even at low alkali on pulp levels. Unlike the consumption curve of bleach KF the consumption curve for bleach DR was normal in appearance and yielded data of kinetic significance. This behavior was probably related to the content of transition metal ion.

TABLE XI

CHANGES IN THE RATE OF CONSUMPTION OF OXYGEN BY KRAFT PULP RICH IN TRANSITION METAL ION WITH TIME AND ALKALINITY[b]

	DH	DM	DR	Apparent Order[a]
Alkali on pulp, %	6.6	3.3	1.7	--
Initial rate, g. O_2/100 g. pulp/min.	0.192	0.110	0.012	0.7
15-Min. rate, g. O_2/100 g. pulp/min.	0.0335	0.0162	0.0113	0.9
30-Min. rate, g. O_2/100 g. pulp/min.	0.0036	0.0024	--	--
Total consumption at 120 min., g. O_2/100 g. pulp/min.	2.00	0.925	0.620	--

[a]The order of the different time intervals was determined by plotting the rate of oxygen consumption at a given time against the initial alkali in Equation (13).
[b]The pulps were bleached with 130 p.s.i.g. oxygen at 100°C. for 120 minutes.

The calculation of the order of dependence of the oxygen consumption on both the initial alkalinity and hydroxyl ion concentration of the system indicated an apparent first-order reaction throughout a wide time interval as did the behavior of the K-series of pulps. The amount of oxygen ultimately consumed was

also greater than the K-series and the pH of the bleaching solutions (Table XII) dropped very rapidly to values less than in the previous case. This was probably due to the larger production of organic acids. (Compare Tables XII and II.)

TABLE XII

CHANGES IN THE ALKALINITY AND THE CARBONATE FORMATION DURING BLEACHING OF SOUTHERN PINE KRAFT PULP CONTAINING 252 P.P.M. TRANSITION METAL ION[a]

	DH	DM	DK
Alkali applied	6.6	3.3	1.7
Initial (after heating to temperature), pH	12.0	11.7	10.9
15-Minute reaction, pH	9.8	9.2	9.4
30-Minute reaction, pH	9.7	9.5	9.4
60-Minute reaction, pH	9.5	9.5	9.4
120-Minute reaction, pH	9.6	9.5	9.4

[a]The pulps were bleached with 130 p.s.i.g. oxygen at 100°C.

The pH of the sodium hydroxide diminished from a value of about 14 to 9.5 in 15 minutes and in some subsequent experiments was less than 10 in 5 minutes. Titrations showed that little sodium hydroxide was present after 5 minutes and that the sodium ion was present as salts of carbonic and organic acids. Using other softwood kraft pulps, it was found that the sodium carbonate was not effective with oxygen under these conditions of reaction. The continued reaction of the pulp with oxygen even after significant consumption of hydroxide ion is consistent with the earlier speculation that a reactive intermediate (probably lignin phenolates and enolates) are formed initially with alkali and that these react further with oxygen.

The physical properties of the pulps cooked for 120 minutes at three different initial alkali concentrations are dependent upon the initial alkali content as was noted for the pulps which were relatively free of transition metal ion. The properties are all inferior to those of the previous K-series of pulps and reflect the harmful action of the contaminants. It is quite likely that the metal ions are in more intimate contact with the pulp than is the magnesium stabilizer. The properties of these pulps together with the properties of the corresponding low transition metal ion content pulps are given in Table XIII. It is interesting to note that, although pulps DR and KR do not differ greatly in their properties, the pulps DH and KB (bleached with higher alkali) do differ greatly in their chemical and physical properties. An initial lower alkali concentration in oxygen bleaching, therefore, has potential advantages when bleaching a pulp containing these impurities.

TABLE XIII

THE PROPERTIES OF PULPS OF DIFFERENT TRANSITION METAL ION CONTENTS BLEACHED AT DIFFERENT ALKALINITY LEVELS FOR 120 MINUTES, 130 P.S.I. OXYGEN, 100°C.

	DH	DM	DR	KB	KD	KF
Transition metal ion content, p.p.m.	282	252	252	82	82	82
Alkali in pulp, %	6.6	3.3	1.7	6.6	3.3	1.7
Yield, %	88.6	94.9	97.6	93.4	100	99.5
Viscosity, cp.	4.8	7.7	15.0	13.6	17.7	22.2
K-number	6.2	8.9	12.0	6.6	8.1	13.8
α-Cellulose, %	82.6	86.0	88.5	86.7	86.5	87.0
Brightness	42.6	31.1	27.2	45.4	38.0	28.6
Brightness reversion	43.6	34.7	27.6	45.8	38.3	29.2
Zero-span tensile, km.	8.8	11.7	14.1	13.6	14.3	14.7
M.I.T. fold	6	39	81	25	38	27
Tear factor	56.7	122	220	226	243	260
Burst factor	18.9	26.1	26.4	21.6	24.2	20.6

Effect of Bleaching Time

Experiments were also conducted to measure the changes in the pulp properties with respect to time of bleaching in the case of these transition metal-rich pulps. The results, shown in Table XIV, demonstrate that the chemical and physical properties, as before, are determined within the first 15 minutes bleaching. Even the brightness in this case is largely established during these first 15 minutes unlike the behavior of the K-series of pulps during bleaching. The corresponding data for the pulps bleached at 3.3 and 1.7% initial alkali content are shown in the Appendix and they behave in an identical manner to the pulp bleached at 6.6% alkali.

TABLE XIV

THE PROPERTIES OF PULPS RICH IN TRANSITION METAL ION BLEACHED FOR DIFFERENT LENGTHS OF TIME AT 6.6% ALKALINITY, 130 P.S.I. OXYGEN AND 100°C.

	DE	DF	DG	DH
Time, min.	15	30	60	120
Yield, %	92.8	93.2	89.6	88.6
Viscosity, cp.	5.3	4.9	4.7	4.8
K-number	7.3	6.3	6.2	6.2
α-Cellulose, %	83.2	82.6	82.3	82.6
Brightness	39	40.4	41.5	42.6
Brightness reversion	39	40.7	41.7	43.0
Zero-span tensile, km.	8.9	8.6	8.6	8.8
M.I.T. fold	8	6	7	6
Tear factor	70.4	65	64.7	56.8
Burst factor	19.1	18.7	17.8	18.9

Effect of Oxygen Pressure

The effect of pressure on the rate of consumption of oxygen during the bleaching of the pulps rich in transition metal ion was also determined in an effort to gain some understanding of the influence of these ions on the mechanisms which occur during the bleach. It was also hoped to see if the rate of reaction can reflect some dependence upon the rate of solution and of penetration of oxygen into the system. The results of this study are shown in Table XV where the total consumption of oxygen, the rates of consumption of oxygen, and the apparent order of the oxygen consumption are tabulated along with the chemical and physical properties of the resulting pulps. These results indicate that the rate of oxygen consumption initially exhibits an apparent first-order dependence upon the oxygen pressure but this dependence rapidly diminishes to zero order within 15 minutes. This behavior differs from the behavior of the pulps with smaller transition metal ion content (K-series) where the dependence becomes zero order sometime between 15 and 30 minutes reaction. In all likelihood this behavior is related to the corresponding changes in the pH of the bleaching liquor and it is only when the pH is greater than about 10 can the consumption of oxygen be related directly to the oxygen pressure of the system.

The rate of oxygen consumption at 195 p.s.i.g. (bleach DU) was kinetically consistent with the rates of consumptions at lower oxygen pressures. This was not the case for the rate of consumption of oxygen by bleach KP compared to bleaches KB reported earlier. The limited consumption of oxygen by bleach KP (also carried out at 195 p.s.i.g.) cannot be due to the limited availability of oxygen but may be due to the limited availability of oxidation sites. The greater consumption of oxygen by bleach DU (a pulp rich in transition metal ion) could be accomplished if the harmful ions catalyzed a greater oxidation of cellulose and

lignin, an increased production of harmful intermediate peroxide products and an increased concentration of degradation products which were themselves readily oxidized by oxygen. Ultimately, as the reaction proceeds, a situation would be reached when the alkali content was low enough or the pressure of oxygen (quantity of dissolved oxygen) was great enough that the number of reactive oxidizable sites would be the controlling factor in the reaction.

TABLE XV

THE EFFECT OF VARYING OXYGEN PRESSURE ON THE PROPERTIES OF THE D-SERIES OF KRAFT PULPS AFTER BLEACHING[a]

	DS	DT	DH	DU	Apparent Order
Applied pressure, p.s.i.g.	65	97.5	130	195	--
Initial rate, g. O_2/100 g. pulp/min.	0.104	0.125	0.192	0.227	0.9
15-Min. rate, g. O_2/100 g. pulp/min.	0.035	0.030	0.034	0.0032	0
30-Min. rate, g. O_2/100 g. pulp/min.	0.010	0.006	0.009	0.009	0
Total consumption after 120 min. reaction, g. O_2/100 g. pulp	2.0	1.7	2.0	--	--
Yield, %	90.2	90.0	88.6	88.7	--
Viscosity, cp.	4.9	4.5	4.8	4.8	--
K-number	6.7	6.1	6.2	5.3	--
α-Cellulose, %	88.3	88.0	82.6	81.4	--
Brightness	39.4	42.1	42.6	47.6	--
Brightness reversion	39.3	41.8	43.0	46.9	--
Zero-span tensile, km.	8.6	8.1	8.8	7.7	--
M.I.T. fold	6	5	6	5	--
Tear factor	73.9	69.4	56.8	63.5	--
Burst factor	17.3	16.8	18.9	16.5	--

[a]The pulps were reacted at 100°C. for 120 minutes with 6.6% alkali on pulp.

The physical and most chemical properties of the pulps do not exhibit any outstanding sensitivity to limited changes in the oxygen pressure. Increasing pressure tends to decrease properties slightly except for pulp brightness (which is significantly increased as the pressure is increased). The use of different oxygen pressures at different stages of oxygen bleaching is certainly suggested by this behavior if multistage oxygen bleaching is ever adopted.

These results demonstrate that when the amount of transition metal ion is present in excess of that able to be handled by the magnesium ion inhibitor, the effect is to increase the rate of consumption of oxygen. The period over which external parameters influence the consumption has been diminished from somewhat less than 30 minutes to less than 15 minutes. During this initial period, the parameters have the same influence as they had previously as can be seen in the following summary:

$$-\left[\frac{dO_2}{dt}\right] \alpha \, [NaOH]_i^{1*} \, [O_2]^1 \, [M]^1 \qquad (16)$$

where

$[NaOH]^{1*}$ = the initial concentration of alkali

$[O_2]^1$ = oxygen pressure

$[M]$ = transition metal ion content.

As the reaction proceeds, these parameters ultimately become zero order due to the decrease of the pH of the bleaching liquor to a value less than 11, and to inherent kinetic relationships which could lead to the ultimate elimination of the effect of the transition metal ion.

This behavior can be rationalized by assuming the formation of enolate and phenolate ions proportional to the applied alkali. Until the pH of the liquor decreases to a value somewhat less than 11, these ions will react with

oxygen to produce hydrogen peroxide, organic peroxides, various organic radicals, and, in some cases, even additional peroxide precursors. Although bleaching and degradation of lignin occur, the various radicals and peroxides also react with the polysaccharide components of the pulp in a manner harmful to the viscosity and to the physical properties of the pulp. As the pH of the liquors increases and the content of suitable organic ions decreases, further oxygen consumption becomes independent of the parameters investigated here. In the presence of certain transition metal ions such as iron, cobalt, and copper, catalysis encourages the decomposition of the peroxides by a radical mechanism whose products also react with the polysaccharide components of the pulp in a harmful manner. The effect of the transition metal ion is limited to the initial period of the bleach and although this behavior might be due to changes in caustic concentration, it is thought instead to be related to the mechanistic behavior of the system as was found to be the case in certain model studies.

It is obvious that those factors which influence the formation and behavior of the peroxidic components in the bleach have a profound influence on its outcome. The decomposition of the peroxide can be controlled by suitable additives, but whether these were properly employed here is not yet known. Lignin is most likely the principal source of peroxides. It is possible that techniques to control the production of peroxide can be devised if significant differences between the reactions of lignin and of polysaccharides can be detected.

Variations in Magnesium Salt Stabilizers

It was conjectured earlier that the effectiveness of the magnesium carbonate treatment of the pulps rich in transition metal ion was not great. This was confirmed by bleaching pulp series-D in the total absence of added magnesium salts. The results, shown in Table XVI, indicate only a slightly

poorer product than the stabilized control. It is likely, therefore, that the magnesium ion was not able to penetrate into the fiber to prevent the harmful action of the resulting hydrogen peroxide intermediate.

TABLE XVI

THE EFFECT OF THE PRESENCE OR ABSENCE OF MAGNESIUM SALTS ON THE PROPERTIES OF SOUTHERN PINE KRAFT PULP AFTER OXYGEN BLEACHING[a]

	DH	DW
$MgCO_3$ on pulp, %	1	0
Initial rate, g. O_2/100 g. pulp/min.	0.192	0.227
15-Min. rate, g. O_2/100 g. pulp/min.	0.034	0.037
30-Min. rate, g. O_2/100 g. pulp/min.	0.009	0.008
Total consumption after 120 min. reactions, g. O_2/100 g. pulp	2.0	2.1
Yield, %	88.6	91.3
Viscosity, cp.	4.8	4.0
K-number	6.2	5.1
α-Cellulose, %	82.6	82.0
Brightness	42.6	47.8
Brightness reversion	43.0	46.3
Zero-span tensile, km.	8.79	7.62
M.I.T. fold	6	4
Tear factor	56.8	49.3
Burst factor	18.9	15.9

[a]The pulps were reacted with 6.6% alkali, 130 p.s.i.g. oxygen at 100°C. for 120 minutes.

Experiments were, therefore, undertaken to improve the penetration of the magnesium ion into the fiber and, in doing so, the necessary changes in procedure made it impossible to compare these new bleaches directly with the previous bleaches. The results shown in Table XVII indicate that magnesium carbonate limits oxygen consumption only slightly and that the equivalent quantity

of magnesium ion precipitated into the mass of the fiber from the magnesium acetate in a more intimate manner is more effective in limiting oxygen consumption and chemical degradation. None of these improvements, however, is comparable to the pulp not contaminated with transition metal ion. The magnesium ion not only limited consumption of oxygen and the degradation of the pulp, but it also slightly inhibited the removal of lignin.

TABLE XVII

THE EFFECT OF DIFFERENT MAGNESIUM SALTS ON THE PROPERTIES OF SOUTHERN PINE KRAFT PULP AFTER OXYGEN BLEACHING[a]

	DZ	DY	DX	DZ
Stabilizer	$Mg(OAc)_2$	$MgCO_3$	$MgCO_3$	None
$MgCO_3$ on pulp, %	1	1	1/2	0
Initial rate, g. O_2/100 g. pulp/min.	0.139	0.167	0.139	0.178
15-Min. rate, g. O_2/100 g. pulp/min.	0.048	0.048	0.048	0.042
30-Min. rate, g. O_2/100 g. pulp/min.	0.003	0.003	0.012	0.012
Total consumption after 120 min. reaction, g. O_2/100 g. pulp	2.0	2.0	2.0	2.0
Yield, %	88.6	87.4	88.3	88.3
Viscosity, cp.	4.7	4.3	4.3	4.0
K-number	6.1	5.8	5.7	5.1
α-Cellulose, %	83.1	82.8	82.6	82.0
Brightness	45.8	44.4	45.6	52.0
Brightness reversion	45.7	43.9	44.8	49.6
Zero-span tensile, km.	8.4	8.5	8.2	7.7
M.I.T. fold	7	5	4	4
Tear factor	79.0	67.9	58.4	47.8
Burst factor	17.9	17.8	16.1	16.0

[a]The pulps were reacted with 6.6% alkali, 130 p.s.i.g. oxygen at 100°C. for 120 minutes.

THE BEHAVIOR OF CELLULOSE DURING OXYGEN BLEACHING

The cellulose sample employed here is a second cut linters, dewaxed, free of pectin, bleached and containing less than 0.05% ash prepared by Hercules. Its behavior during oxygen bleaching is summarized in Table XVIII. The curves from which these data were obtained showed a pronounced induction period before the consumption of oxygen became appreciable. After this interval, the rate of consumption of oxygen and the total consumption of oxygen increased greatly but only after 90 minutes did the consumption at highest alkali levels become proportional to the applied alkalinity. The low consumption of oxygen and the very pronounced induction periods shown in Fig. 4 were not typical of kraft pulps. Because of the lack of data, it is impossible to compare these results with the results of Michie and Neale (35). Those viscose aging experiments showed cellulose to be degraded in a very complex manner in which the loss of oxygen occurred as follows:

$$\frac{-dO_2}{dt} = k\,[\text{cellulose}]^{1.35}[\text{NaOH}]\,\frac{[O_2]}{k^1 + [O_2]}\,p\,[M] \qquad (17)$$

where k and k^1 are constants and $p[M]$ is related to the concentration of the transition metal ion content.

TABLE XVIII

THE REACTION OF CELLULOSE WITH OXYGEN UNDER THE CONDITIONS OF THE OXYGEN BLEACH[a]

	FA	FB	FC
Alkalinity, %	6.6	3.3	1.7
Type of oxygen consumption	induction	induction	induction
Total consumption of oxygen, g. O_2/100 g. sample	0.37	0.33	0.20
Yield, %	97.5	94.8	99.6
Viscosity (initial viscosity = 11.8), cp.	4.7	5.0	6.5

[a]At 130 p.s.i.g. oxygen, 100°C., 120 minutes reaction.

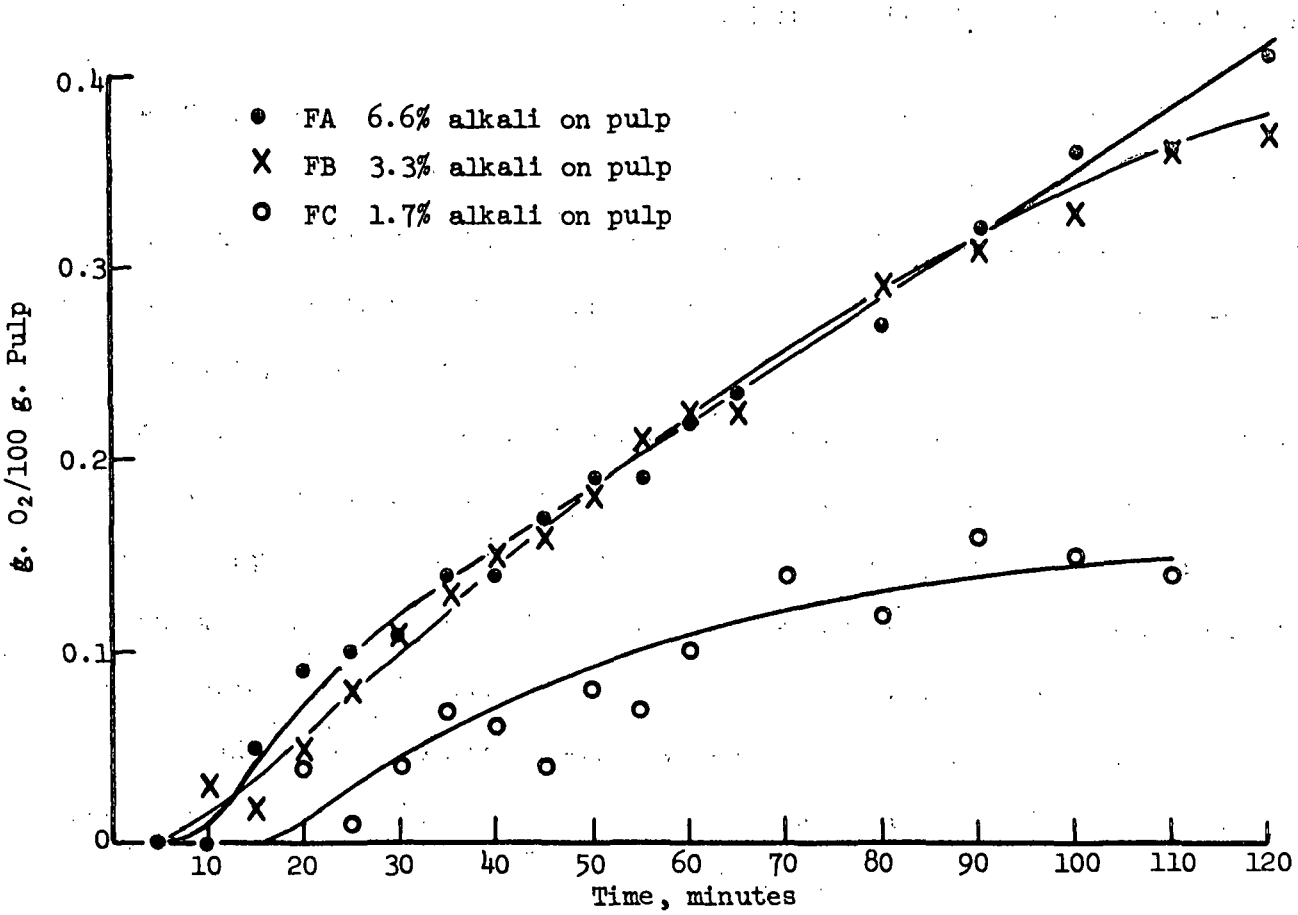


Figure 4. The Reaction of Cotton Linters with Oxygen (130 p.s.i.g.) at 100°C. at Different Alkalinities

Thus, a basic difference between the lignified and nonlignified pulps seems to be the existence of an induction period before rapid consumption of oxygen occurs. The short induction-like periods observed in the case of a certain few lignified pulps may be related to the small alkali content caused by the partial consumption of alkali by organic acids.

THE BEHAVIOR OF CHLORITED KRAFT PULPS DURING OXYGEN BLEACHING

A large quantity of the commercially prepared southern pine kraft pulp was bleached with sodium chlorite acidified to pH 4 at room temperature for long but varying periods of time. Samples were removed at three time intervals, washed

free of oxidizing agent with water, centrifuged to a high consistency and stored in a refrigerator. The analysis of these pulps is given in Table XIX. The pulps should theoretically differ only in the amount and type of lignin present since the mild room temperature chloriting conditions cause only a minimum of degradation. Little change should occur in the structure of the cellulosic component, and any that does will be the same for all since changes in salt concentration, not time of trea ment, is the major cause of such alterations (36). This prolonged treatment has brought about some degradation since the pulp viscosities were reduced significantly from the original value of 29.0. The chloriting process itself introduced small amounts of carboxylic acid groups into the pulp (37). A transition metal ion content of 107.4, and 148.3 p.p.m. was present in bleached pulps H, and J, respectively.

TABLE XIX

THE CHEMICAL COMPOSITION OF CHLORITED SOUTHERN PINE KRAFT PULP

Pulp designation	H	J	G
Time of bleaching, days	3	6	14
Brightness	32.1	44.2	72.6
Brightness reversion	31.8	44.1	76.7
Viscosity, cp.	26.2	26.5	21.0
K-number	18.0	6.5	1.2
Metal analysis			
Ba, p.p.m.	0.33	0.5	
Ca	884	1824	
Mg	265	552	
Sr	10	18	
Na	34	69	
B	0.48	0.34	
Al	18	26	
Si	44	45	
Pb	3.4	8.1	
Cu	52	104	
Fe	22	38	
Ti	3.2	5.8	
V	0.24	0.52	

The most highly chlorited G-series of pulp was bleached with oxygen at 130 p.s.i. and 100°C. for 120 minutes with different initial alkali concentrations as shown in Table XX and Fig. 5. The rate of consumption of oxygen showed a behavior similar to the previous bleaches (E-series) with an initial rapid increase followed by a declining rate of oxygen consumption. There was no simple apparent order with respect to alkali applied to the bleach. The reactions are, therefore, more complex than those encountered previously. This is possibly due to the changed nature of the lignin and to the introduction of degradation sites into the cellulose.

TABLE XX

THE REACTION OF HIGHLY CHLORITED SOUTHERN PINE KRAFT PULP WITH OXYGEN UNDER THE CONDITIONS OF THE OXYGEN BLEACH[a]

	GA	GB	GC
Alkali on pulp, %	6.6	3.3	1.7
Initial rate, g. O_2/100 g. pulp/min.	0.026	0.021	0.025
15-Min. rate, g. O_2/100 g. pulp/min.	0.020	0.013	0.011
30-Min. rate, g. O_2/100 g. pulp/min.	0.017	0.007	0.002
Total consumption after 120 min. reaction, g. O_2/100 g. pulp	1.3	0.7	0.6
Yield, %	94.2	97.7	100.8
Viscosity, cp.	3.6	5.6	8.2
Brightness	87.1	84.6	81.6
Brightness reversion	85.4	81.5	80.9
Zero-span tensile, km.	9.9	10.0	12.8
M.I.T. fold	3	11	20
Tear factor	54.3	100	171
Burst factor	14.2	19.9	21.5

[a]At 100°C., 130 p.s.i.g. oxygen, 120 minutes reaction.

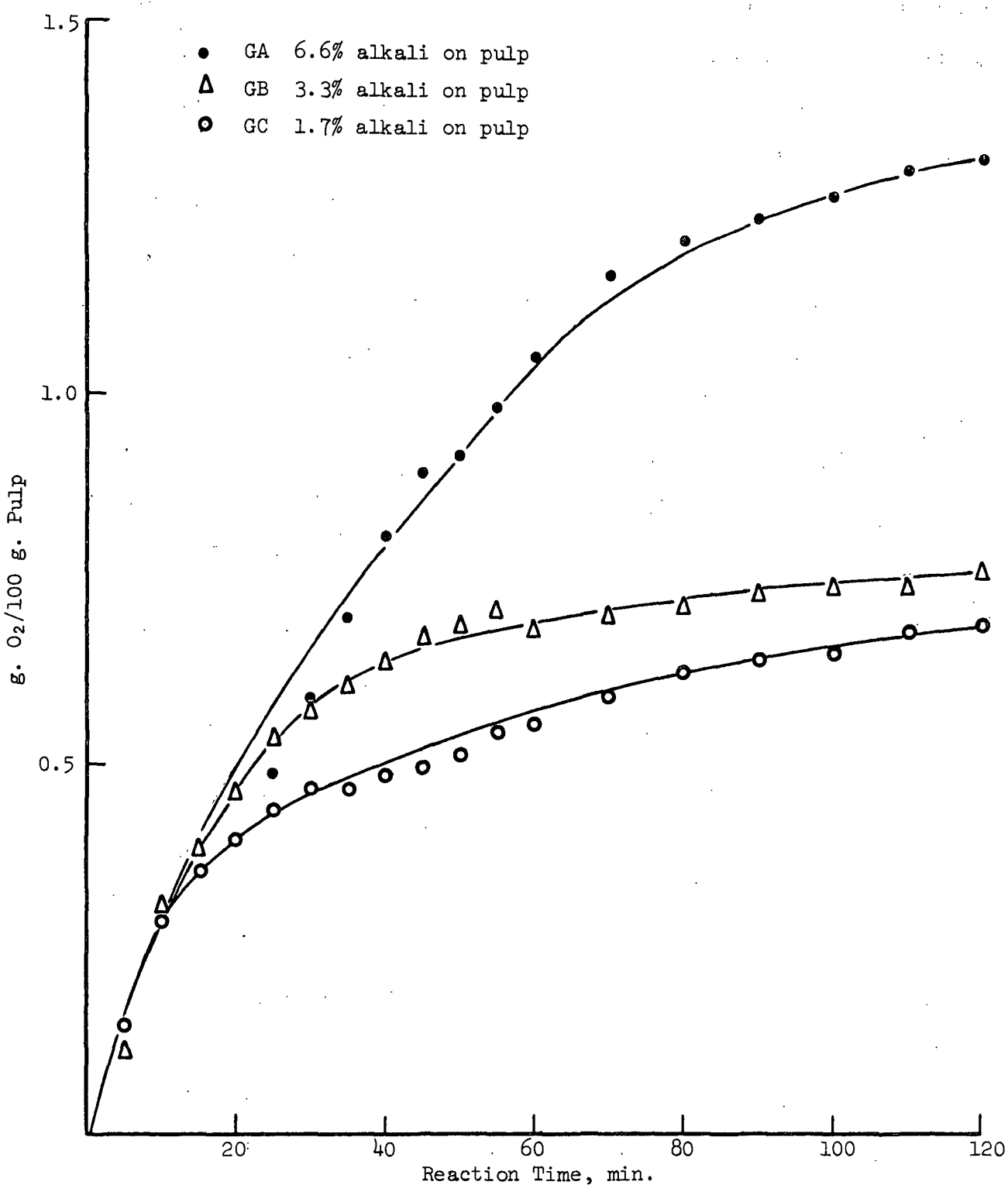


Figure 5. The Reaction of Chlorite Bleached Southern Pine Kraft Pulp (Series G) with 130 p.s.i.g. Oxygen at 100°C. and Different Alkali-to-Pulp Ratio

The chemical and physical properties of the G-series of pulps are also given in Table XX. The drastic reduction in the viscosity of the pulp from 21 to very low values after bleaching suggests that the chloriting procedure has introduced many alkali-labile centers into the polysaccharide component of the pulp. The chemical nature of these sensitive linkages is not known but might include carbonyl groups within the cellulose chains. In these bleaches as in all others, the properties of the pulps are altered by an amount related to the applied alkali. As can be seen in Table XXI and Fig. 5, the rate of consumption of oxygen could not be related to the initial alkali concentration through any simple kinetic relationship. No kinetic significance may be attached to this behavior because the chloriting procedure has changed both the quantity and the chemical nature of the lignin in the pulp. As in previous bleaches, the pH of the bleaching system decreased from near 12 to about 9.5 to 10 in less than 15 minutes.

The physical properties of the J-series of pulps were most adversely affected by bleaching at the highest (6.6%) level of alkalinity. Significant brightness gains were achieved at the lower alkalinity levels of bleaching without causing excessive degradation. Thus, an oxygen stage might be used as an intermediate bleaching stage in a complex bleaching system if low alkali to pulp ratios during the bleach were employed.

The most mildly chlorited kraft pine pulps (labeled Series H) had a permanganate number of 13 and a viscosity of 26.6. The consumption of oxygen by these pulps at the three alkalinity levels resembled that of the various kraft pulps studied earlier. No evidence of an induction curve was observed in Fig. 6. The total consumption of oxygen was proportional to the applied alkali and the rate of consumption of oxygen (shown in Table XXII) during the bleach could be related to the applied alkali through complex but constant

kinetic relationship. The patterns of behavior of the chemical and physical properties of these pulps are summarized in Table XXII and are similar to those reported for the behavior of Series G and J.

TABLE XXI

THE REACTION OF MODERATELY CHLORITED SOUTHERN PINE KRAFT PULP WITH OXYGEN UNDER THE CONDITIONS OF THE OXYGEN BLEACH[b]

	JA	JB	JC
Alkali on pulp, %	6.6	3.3	1.7
Initial rate, g. O_2/100 g. pulp/min.	0.024	--[a]	--[a]
15-Min. rate, g. O_2/100 g. pulp/min.	0.013	0.003	--[a]
30-Min. rate, g. O_2/100 g. pulp/min.	0.008	0.001	--[a]
Total consumption after 120 min. reaction, g. O_2/100 g. pulp	0.75	0.12	0.10
Yield, %	92.5	96.6	98.6
Viscosity, cp.	6.8	12.3	19.1
K-number	1.6	2.1	2.7
α-Cellulose, %	86.3	87.7	87.2
Brightness	72.0	63.5	58.4
Brightness reversion	71.6	63.4	58.2
Zero-span tensile, km.	10.7	13.6	14.3
M.I.T. fold	16	34	39
Tear factor	154	266	258
Burst factor	17.4	21.0	22.9

[a] No value could be obtained because of induction effects.

[b] At 100°C., 130 p.s.i.g. oxygen, 120 minutes reaction.

The reaction of pulp with oxygen and alkali is profoundly affected by the lignin component of the pulp. These qualitative experiments suggest that not only is the quantity of lignin significant but that its chemical nature as modified by the previous pulping and bleaching stages is also important. In

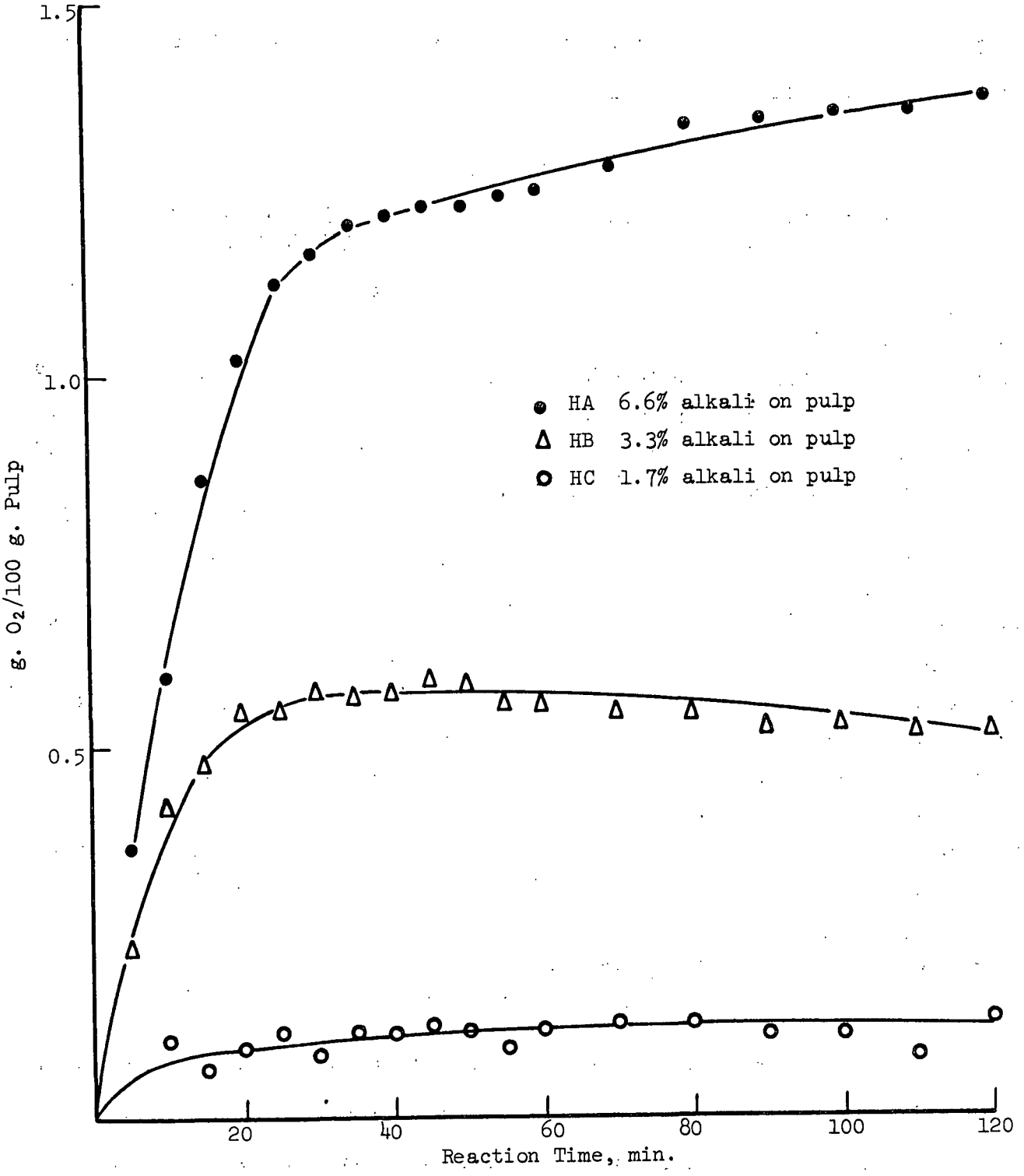


Figure 6. The Reaction of Partially Chlorited Southern Pine Kraft Pulp (Series H) with 130 p.s.i.g. Oxygen at 100°C. and Different Alkali-to-Pulp Ratios

some instances the empirical kinetic patterns observed for the unmodified unbleached pulp have been completely altered. Nevertheless, these results, combined with the reaction of cotton with oxygen and alkali suggest that the reactions of lignin and cellulose follow completely different mechanisms.

TABLE XXII

THE REACTION OF MILDLY CHLORITED SOUTHERN PINE KRAFT PULP WITH OXYGEN UNDER THE CONDITIONS OF THE OXYGEN BLEACH[a]

	HA	HB	HC	Apparent Order
$MgCO_3$ on pulp, %	6.6	3.3	1.7	--
Initial rate, g. O_2/100 g. pulp/min.	0.100	0.036	0.010	1.4
15-Min. rate, g. O_2/100 g. pulp/min.	0.030	0.009	--[b]	1.5
30-Min. rate, g. O_2/100 g. pulp/min.	0.008	0.002	--[b]	1.5
Total consumption after 120 min. reaction, g. O_2/100 g. pulp	1.36	0.58	0.12	--
Yield, %	90.7	95.8	96.2	--
Viscosity, cp.	5.9	10.6	18.6	--
K-number	3.7	4.8	6.0	--
α-Cellulose, %	84.6	84.5	83.3	--
Brightness	59.9	50.1	43.0	--
Brightness reversion	60.2	50.8	43.4	--
Zero-span tensile, km.	10.4	13.1	13.9	--
M.I.T. fold	12	26	33	--
Tear factor	128	221	267	--
Burst factor	17	21.2	20.5	--

[a]At 100°C., 130 p.s.i.g. oxygen, 120 minutes reaction.

[b]Too small to measure.

The reaction of pure cellulose may be pictured as a slow oxidation of alcohol groups (chiefly secondary) with oxygen to yield a degraded cellulose of unknown nature and hydrogen peroxide. The hydrogen peroxide reacts in a complex manner to set up a chain radical degradation of cellulose. The length of the chain will depend upon the concentration of "stopping" reactants. An induction period is present due to the slow "build-up" of peroxide concentration. The unknown degraded cellulose structure probably reacts with alkali according to the chain cleaving mechanism proposed by Brooks and Thompson (21).

The enolate or phenolate form of lignin, on the other hand, reacts rapidly with oxygen to yield degraded lignin, additional hydrogen peroxide precursors and hydrogen peroxide. Although an induction period before the onset of the maximum rate of oxygen consumption might conceivably occur, the great reactivity of lignin to oxygen puts this period well within the range of experimental error. The rapid build-up of peroxide content from lignin reactions is manifested in a rapid degradation of the cellulosic component of the pulp as the amount and type of lignin increases. By limiting the production of the peroxide generated by lignin, it might be possible to minimize cellulose degradation.

In order to eliminate the possibility that purely physical factors accounted for the differences in bleaching behavior between lignin-rich pulps and cotton linters, a fully bleached southern pine kraft pulp prepared by Champion Papers was bleached under the conditions of oxygen bleaching employed here. This pulp had a permanganate number of 0.8 and the rate of consumption of oxygen is shown in Table XXIII and Fig. 7. The data show that, here too, induction periods occur before the rate of consumption of oxygen becomes appreciable. In all likelihood, the induction period is related to the conjectured fewer number of peroxide precursors in the pulp brought about by the

very high degree of delignification. Here too, the rate of consumption of the oxygen is no longer dependent in a simple manner on the initial alkali concentration and although the reason is not proven, it might be due to the sensitization of cellulose to oxygen during commercial bleaching.

TABLE XXIII

THE REACTION OF COMMERCIALLY BLEACHED SOUTHERN PINE PULP WITH OXYGEN AND ALKALI[a]

	EA	ER	EC	Unoxidized Control
$MgCO_3$ on pulp, %	6.6	2.3	1.7	--
Initial rate, g. O_2/100 g. pulp/min.	induction	induction	induction	--
Total consumption after 120 min. reaction, g. O_2/100 g. pulp	0.8	0.25	--	--
Yield, %	90	96.8	99.2	--
Viscosity, cp.	4.7	7.8	9.6	13.2
K-number	--	--	--	--
α-Cellulose, %	85.2	86.0	86.0	--
Brightness	88.4	86.5	85.7	85.6
Brightness reversion	87.0	85.9	94.5	83.8
Zero-span tensile, km.	8.5	11.5	12.8	13.6
M.I.T. fold	5	13	15	12
Tear factor	92.8	177	229	248
Burst factor	13.7	16.0	18.6	16.9

[a]With 130 p.s.i.g. oxygen, 100°C., and for 120 minutes.

EFFECT OF BLEACHING ON THE CHEMICAL AND PHYSICAL PROPERTIES OF PULPS

The reaction of pulp with oxygen in the presence of alkali occurs in general terms, by three main reactions, namely: delignification, color removal, and polysaccharide degradation. The latter reaction is associated in some as yet uncertain manner with the changes in many of the physical properties of

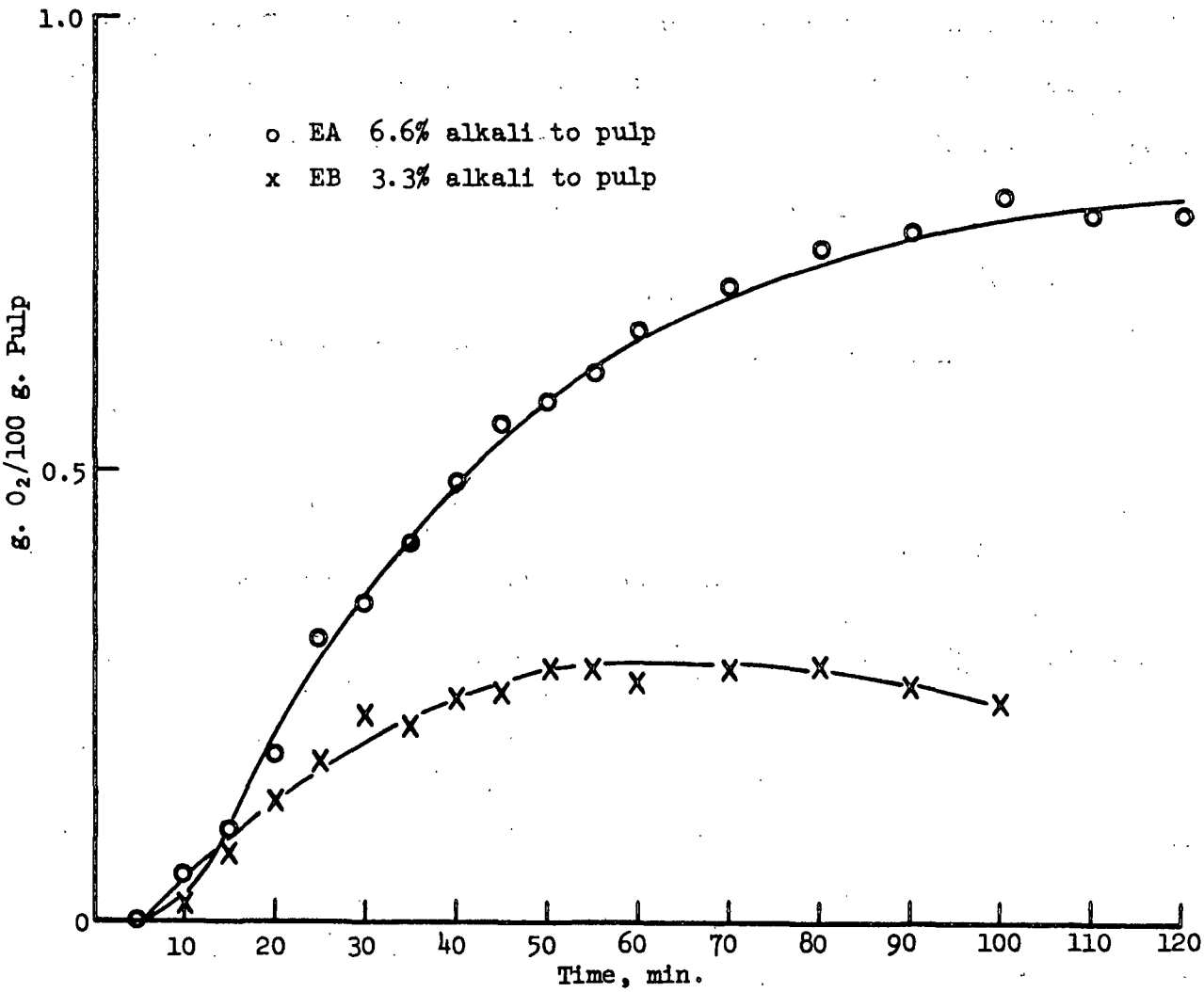


Figure 7. The Reaction of Commercially Bleached Southern Pine Kraft Pulp with 130 p.s.i.g. Oxygen at 100°C. and Various Alkali-to-Pulp Ratios

the pulps. The effect of different parameters upon the parallel reactions of delignification and polysaccharide degradation are plotted in Fig. 8. The comparison between the permanganate number and the pulp viscosity represents a comparison between an approximation of the lignin removal and of the chain-cleavage degradation reactions. Such a comparison in Fig. 8 indicates that bleaches carried out involving modest differences of alkalinity and times of reaction may be forced onto one relatively smooth curve. This result is

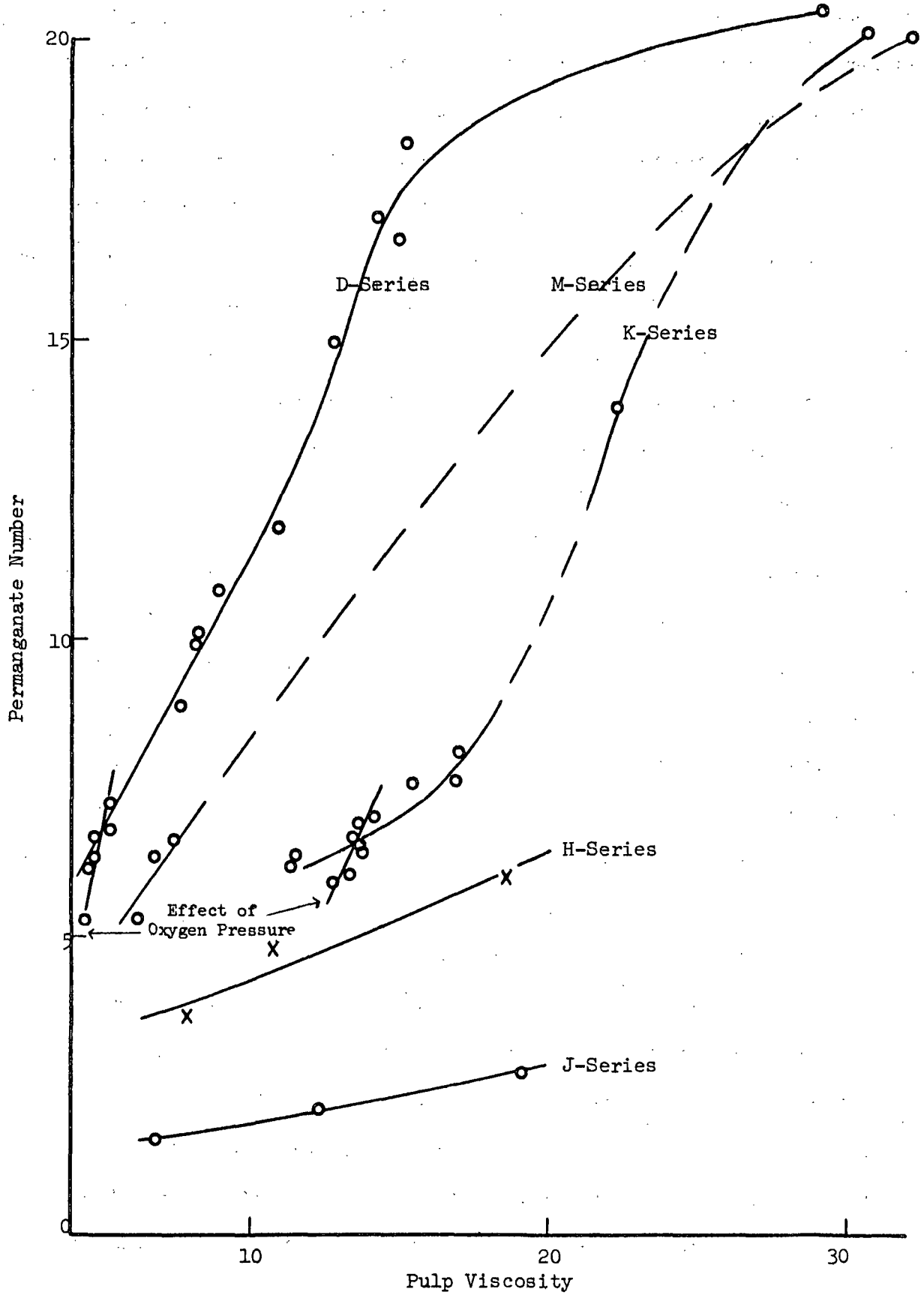


Figure 8. A Comparison of the Permanganate Number and Pulp Viscosity of Southern Pine Kraft Pulps Bleached with Oxygen

consistent with those obtained earlier by Norrstrom and others (37,38). On the other hand, the same relationships for otherwise identical pulps having different transition metal ion contents (going from Series D to M to K) cannot be forced into the same curve discussed above since these ions catalyze the decomposition of polysaccharides at a greater rate than they cause the removal of lignin. The removal of lignin before oxygen bleaching (going from Series M to H to J) also gives a series of separate curves for each lignin level with viscosity being more adversely affected as lignin is removed. This effect was conjectured to be due to the introduction of peroxide precursors into both the lignin and the cellulose. An increase in oxygen pressure during bleaching, on the other hand, increases lignin removal relative to polysaccharide degradation.

The plots also suggest that the transition metal ion has its most harmful effect on pulp viscosity at higher lignin contents and this may be either a reflection of the difficulty of penetration of the magnesium ion stabilizer into the pulp and/or the production of greater amounts of hydrogen peroxide with its concomitant catalytic decomposition by the undesirable radical pathway at the higher lignin levels. At lower transition metal ion contents, the initial cellulose degradation is not as great at higher lignin contents as the previous example and delignification occurs more rapidly than degradation. Although the production of hydrogen peroxide may be just as great as previously, less catalyst is present to encourage its decomposition by the radical mechanism. At lower lignin levels, whether produced by oxygen bleaching or by chlorite delignification, pulp degradation occurs more rapidly than delignification. This behavior may reflect the cumulative build-up of hydrogen peroxide during the bleach to such levels that the small quantity which is decomposed by the radical mechanism becomes significant and/or that the last traces of lignin are increasingly difficult

to remove, necessitating prolonged bleaching conditions. In the case of pulp Series H and J, the chloriting process has probably introduced carbonyl groups into the polysaccharide component which would be points of hydrogen peroxide formation. These groups might also be formed as a result of prolonged oxygen bleaching in this case and would thereby account for the flattening curve of pulp Series K.

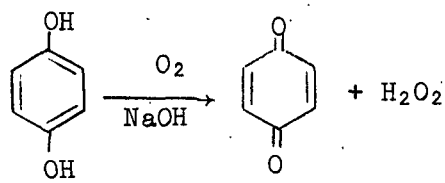
The plots suggest that oxygen bleaching is potentially most effectively used on pulps with high lignin contents free of transition metal ion and that the relatively soft kraft pulp employed here was not the most ideal starting material. Elimination of the harmful intermediate compounds of these higher yield pulps combined with less extensive delignification should yield results of much more practical significance. Alternatively, partial delignification of high yield pulps using other bleaching agents followed by an oxygen bleach could be successful if the peroxide precursors were reduced to a minimum.

The plots of the relationship between the permanganate number (lignin content) and the pulp brightness (chromophore content) show that there is less dependence upon transition metal ion content and a greater dependence upon oxygen pressure of the system. This is expected since the color of pulp is associated with its lignin content. The relationships plotted on the previous Fig. 8 show a greater sensitivity to variations in the bleaching procedure than do those derived from the plots of permanganate number vs. brightness.

Because of the different effect of parameters on the bleaching and the degradation reactions, it may be possible to optimize one at the expense of the other. This optimization may occur through the elimination, stabilization or otherwise neutralization of the hydrogen peroxide or its precursors as mentioned previously. Many techniques have already been developed for this purpose. Control

of the radical decomposition of the peroxide by the addition of suitable magnesium salts in an effective manner, the use of substances to encourage an ionic decomposition of the peroxide (by the addition of iodide ion, sulfur or polysulfides) and possibly through the removal of the hydrogen peroxide precursors from both the polysaccharide and the lignin components of the pulp are examples of this. The existence of induction periods before the onset of rapid oxygen consumption (and during the period of greatest chemical and physical property sensitivity to the bleach) suggests that a multistage process might be feasible. Thus, numerous possibilities are available which might lead to an improved oxygen bleaching technology.

A series of experiments were directed to determining whether improvements in the pulp viscosity to delignification ratio could be achieved by modifying the bleaching process to remove the more reactive hydrogen peroxide precursors. These reactive precursors are as yet largely unknown but can include carbonyls such as those in glucose (9) or reducing end groups, other types of carbonyls, and quinones such as those derived from hydroquinone. McCloskey has shown that hydroquinone, a known stabilizer of cellulose during alkali aging (11,39) catalyzes the decomposition of methyl β-D-glucoside under the conditions of oxygen bleaching and could degrade cellulose in a similar manner through the production of hydrogen peroxide (46). These structures, often associated with lignin, together with aliphatic or other structures capable of forming unstable hydroperoxides, could



yield hydrogen peroxide capable of degrading cellulose. The removal of these components by chemical (e.g., oxidation and/or reduction) or physical (multi-stage or sequential bleaching) means could minimize pulp degradation.

CHEMICAL ALTERATION OF KRAFT PULP FOR BLEACHING

Pulp Series J was chosen for the first experiment in this series since it had been oxidized with acidified sodium chlorite in such a manner that, although significant amounts of lignin had been removed, large quantities still remained in an oxidized condition. A large batch of Pulp J was extracted with 0.1N NaOH and a portion of it (wet with alkali) was reduced with sodium borohydride. The pulps were then bleached with 130 p.s.i. oxygen at 100°C., 6.6% alkalinity for 120 minutes. The rate of consumption of oxygen by these pulps and their controls is given in Table XXIV.

TABLE XXIV

THE REACTION OF MODIFIED CHLORITED KRAFT PULPS WITH OXYGEN UNDER THE CONDITIONS OF AN OXYGEN BLEACH[a]

	MA	JA	JF	JE
Chlorited	No	Yes	Yes	Yes
Extracted (0.1N NaOH)	No	No	Yes	Yes
Reduced ($NaBH_4$)	No	No	No	Yes
K-number before treatment	29.5	6.5	4.4	4.4
Initial rate, g. O_2/100 g. pulp/min.	0.110	0.024	induction	induction
15-Min. rate, g. O_2/100 g. pulp/min.	0.016	0.013	0.016	0.005
30-Min. rate, g. O_2/100 g. pulp/min.	0.002	0.008	0.006	0.003
Total consumption after 120 min. reaction, g. O_2/100 g. sample	1.66	0.75	0.50	0.17

[a]At 100°C., 130 p.s.i.g. oxygen, 6.6% alkali on pulp for 120 minutes.

The results (in Table XXIV and Fig. 9) demonstrate that the extraction of the substances rendered potentially soluble in dilute NaOH by the chloriting procedure from the pulp, eliminates much of the total consumption of oxygen that otherwise occurs during the bleach. Unlike the original chlorited (unextracted) pulp, the consumption of oxygen now exhibits a slower initial rate of consumption and a lower final total consumption. This changed behavior of oxygen consumption now resembles that of the more highly bleached pulps of Series J and G. The consumption of oxygen during the bleaching of cellulose exhibits an induction period. Extraction of pulp Series J causes this partially bleached pulp to behave in a similar manner, suggesting the extracted lignin (the K-number was decreased to 4.4) contributed to the initial rapid consumption oxygen. The reduction of Pulp JE with $NaBH_4$ will destroy quinones and convert carbonyl groups to alcoholic or phenolic units. The reduced pulp consumes even less oxygen than the extracted pulp. From this observation it can be conjectured that a significant proportion of the remaining unextracted carbonyl groups in the pulps were reduced. The reduced quinones might be expected to be reoxidized to quinones and to then behave as formerly whereas the reduced carbonyls would not be readily reoxidized.

The physical and chemical properties of these pulps and their controls are given in Table XXV and reflect the various chemical and physical manipulations the original pulps have undergone.

Strangely, the extraction of the chlorited pulp with dilute alkali did not result in a pulp with significantly different physical properties after bleaching compared to the unextracted pulp even though great differences in oxygen consumption had occurred. A slight increase in the brightness was observed suggesting the elimination of some chromophoric groups. After reduction with sodium borohydride and bleaching with oxygen, the pulp became considerably brighter and had a

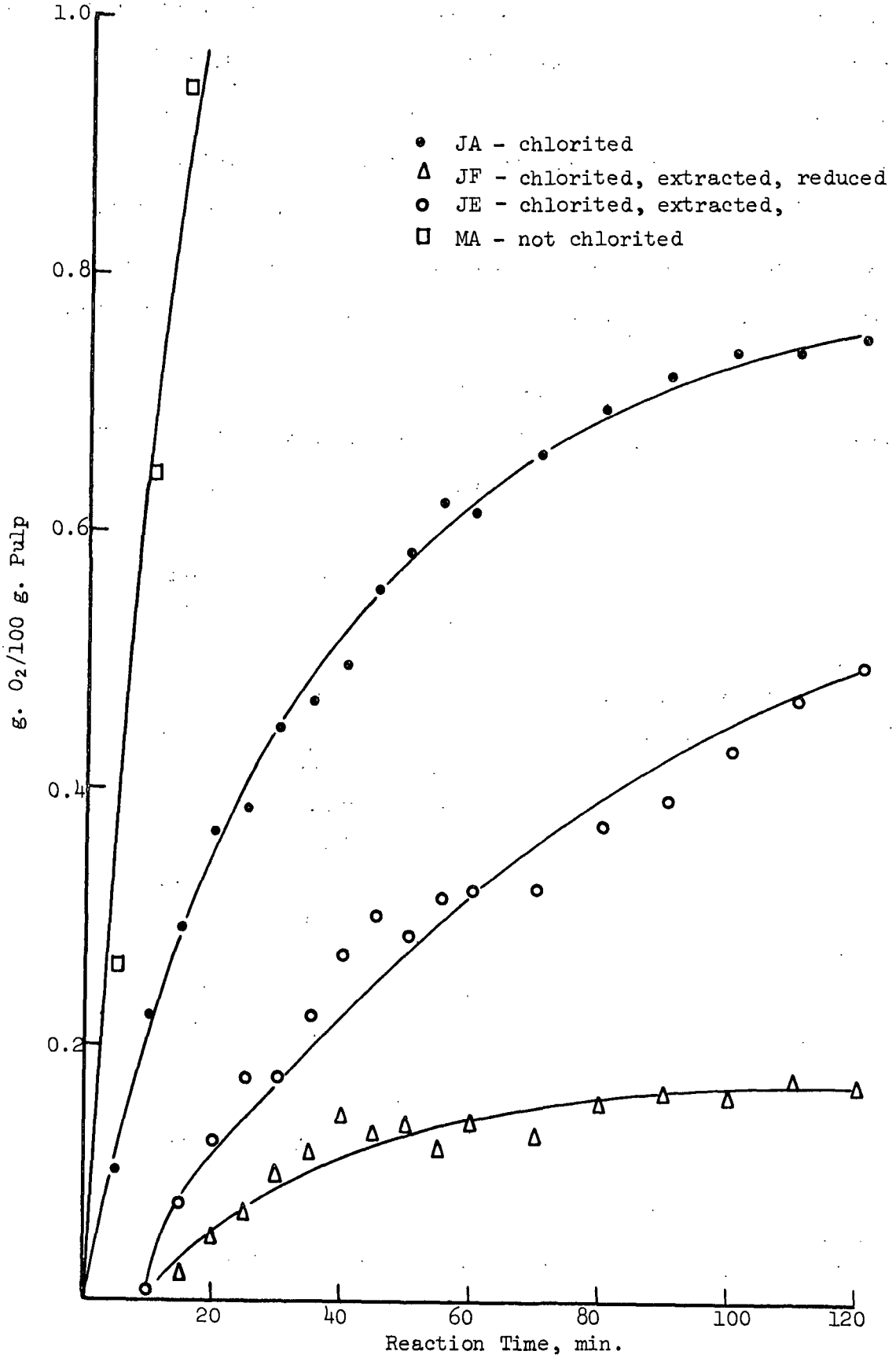


Figure 9. The Reaction of Partially Chlorited Southern Pine Kraft Pulp with 130 p.s.i.g. Oxygen at 100°C. and 6.6% Alkali-to-Pulp Ratio After Various Pretreatments

significantly higher viscosity. At the same time, the tear factor was much higher but the significance of this value obtained only on unbeaten pulp is limited. Since the physical properties of the pulps subjected to oxygen bleaching are determined by the initial alkali concentration within 15 minutes, it is tempting to speculate that the factors within the pulp which control the initial chemical response to bleaching may also have a bearing on the ultimate physical property. The measurement of oxygen consumption alone does not provide the means of measuring this reaction.

TABLE XXV

THE PROPERTIES OF MODIFIED CHLORITED KRAFT PULPS AFTER OXYGEN BLEACHING[a]

	MA	JD	JF	JE
Chlorited	No	Yes	Yes	Yes
Extracted	No	No	Yes	Yes
Reduced	No	No	No	Yes
Bleached with oxygen	Yes	Yes	Yes	Yes
Carbonyl content before treatment	5	7.2	--	--
after treatment	--	2.3	3.3	3.0
Oxygen consumption, g. O_2/100 g. pulp	1.66	0.75	0.5	0.17
Type of consumption	normal	normal	induction	induction
Yield, %	--	92.5	93.6	94.3
Viscosity, cp.	6.4	6.8	6.3	11.6
K-number	5.3	1.6	1.4	1.6
α-Cellulose, %	84.2	86.3	86.9	86.7
Brightness	48.7	72.0	73.5	75.2
Brightness reversion	49.1	71.6	72.5	74.5
Zero-span tensile, km.	10.2	10.7	10.5	12.4
M.I.T. fold	22	16	14	14
Tear factor	116	154	150	231
Burst factor	25.2	17.4	16.4	16.9

[a]At 100°C., 130 p.s.i.g. oxygen, 6.6% alkali on pulp for 120 minutes.

The reduction of semibleached pulps before oxygen bleaching does confer some chemical stability by the removal of functional groups introduced by the bleaching process. Unbleached kraft pulps, on the other hand, which have not been subjected to oxidative action presumably would not contain as many reducible groups capable of producing hydrogen peroxide. In addition to these possible precursors, it would contain condensed lignins (23) less susceptible to oxygen bleaching. The action of reducing agents on unbleached kraft pulp was, therefore, investigated.

A K-series pulp (low in transition metal ion) was extracted with 0.1N sodium hydroxide and a portion of it was bleached with oxygen under standard conditions. Another portion was reduced with sodium borohydride and, after careful washing, was bleached with oxygen as before. The final portion of the extracted pulp was reacted with sodium hydrosulfite (dithionite) under alkaline conditions but otherwise in a manner identical to the bleaching of groundwood. This pulp was also bleached with oxygen after careful washing. The consumption of oxygen by this pulp is shown in Fig. 10 and the properties of the pulps are shown in Table XXVI.

The plot of the consumption of oxygen against time in Fig. 10 shows that extraction of pulp with alkali removes a quantity of oxygen-consuming material. The smaller change in oxygen consumption, compared to the J-series of pulps discussed earlier probably reflects the removal of smaller quantities of lignin. The reduction of the pulp with $NaBH_4$ before bleaching reduces the rate of consumption but does not influence the total consumption of oxygen. The pulp reduced with sodium hydrosulfite reacted the slowest and showed a small induction period. These results coupled with the smaller oxygen consumption demonstrate the possible influence of hydrosulfite bleaching on oxygen consumption. The pulp reduced with sodium hydrosulfite showed a higher viscosity,

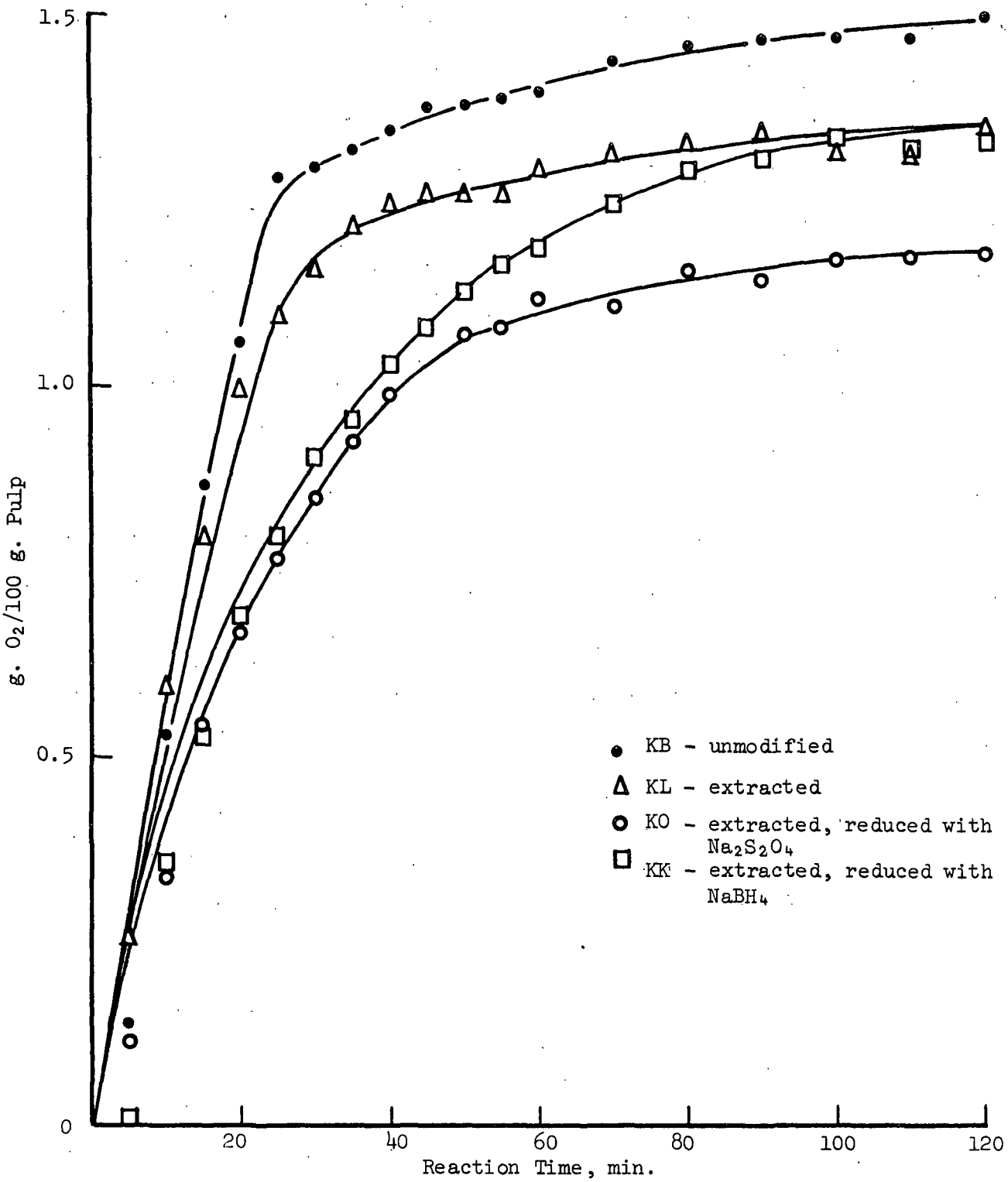


Figure 10. The Reaction of Unbleached Southern Pine Kraft Pulp with 130 p.s.i.g. Oxygen at 100°C. and 6.6% Alkali on Pulp After Various Pretreatments

a greater brightness and a lower lignin content than all other pulps examined in this experiment. This observation coupled with the slightly superior paper properties suggests that the reduction of kraft pulp with hydrosulfite before oxygen bleaching does have a slight beneficial effect.

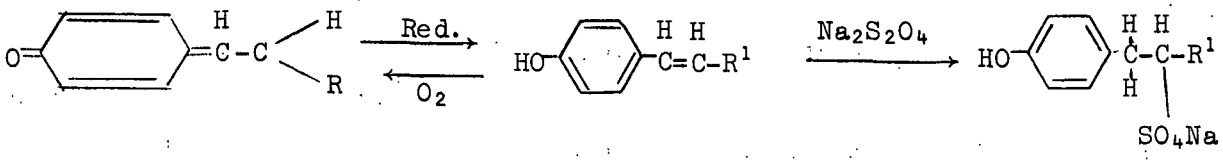
TABLE XXVI

THE BEHAVIOR OF REDUCED UNBLEACHED SOUTHERN PINE KRAFT PULP TO OXYGEN BLEACHING[a]

	Standard Bleach	Alkaline Extracted	Sodium Boro-hydride Reduced	Sodium Hydro-sulfite Reduced
Cook number	KB	KL	KK	KO
Initial rate, g. O_2/100 g. pulp/min.	0.068	0.056	0.049	0.054
15-Min. rate, g. O_2/100 g. pulp/min.	0.043	0.029	0.027	0.026
30-Min. rate, g. O_2/100 g. pulp/min.	0.011	0.010	0.016	0.016
Total consumption after 120 minutes reaction, g. O_2/100 g. pulp	1.50	1.34	1.35	1.18
Yield, %	93.4	92.3	94.6	94.4
Viscosity, cp.	13.6	13.9	13.6	14.7
K-number	6.6	6.4	6.7	6.1
α-Cellulose, %	86.7	87.3	87.1	84.6
Brightness	45.4	48.4	49.0	49.8
Brightness reversion	45.8	48.5	49.3	50.2
Zero-span tensile, km.	13.6	13.7	14.2	14.1
M.I.T. fold	25	23	30	31
Tear factor	226	243	240	267
Burst factor	21.6	21.7	23	21.4

[a]At 6.6% alkali on pulp, 130 p.s.i.g. oxygen, 100°C. for 120 minutes.

The reduction of pulp with sodium borohydride is less effective than sodium hydrosulfite and this result reflects the difference in chemical behavior of these two reagents. Unlike sodium borohydride which can reduce most nonacid carbonyls, sodium hydrosulfite reduces only quinone carbonyl groups quantitatively (39,40) other carbonyl groups slowly (41,42) but it adds to double bonds forming C-S bonds (42,43). It is readily seen that if such an addition occurred to lignin during hydrosulfite bleaching it could, under certain structural considerations, inhibit the oxidation of phenols (reduced quinones) back to the quinone state and lower the quantity of peroxide precursors. This behavior in turn would lower the



production of hydrogen peroxide and decrease the degradation of the pulp. The limited results in the table support this rationalization.

CONCLUSIONS

The results obtained in this investigation suggest that a slow degradation of cellulose and consumption of oxygen occurs when cellulose is reacted with oxygen and alkali at 100°C. This reaction exhibits a complex kinetic pattern with inductive effects which are similar to, but not identical with, the complex radical mechanism known to occur in the case of the aging of cellulose for viscose manufacture. The study of the lignified pulps conducted here demonstrates that lignin reacts rapidly with oxygen and alkali without the appearance of an induction period. Thus, cellulose and lignin exhibit radically different patterns of reaction. These differences of behavior on the part of the pulp components are not as susceptible to technological manipulation as are the differences in existing pulping processes, for example, because of the fact that the reactions of lignin and cellulose with oxygen share a common highly degradative intermediate, chiefly hydrogen peroxide. Since the induction period characteristic of cellulose degradation depends on the production of that intermediate, it will become shorter in pulping reactions due to the introduction of additional peroxide as a result of lignin degradation. Thus, the key to successful oxygen bleaching or pulping lies in the successful elimination or control of the hydrogen peroxide formed during the process. In all likelihood this problem will not be simple and will involve considerable time and expense before it is solved.

The present investigation suggests many avenues of approach which could be successful if the rationalizations of bleaching behavior employed here are significant. The direct approach of attempting to prevent the peroxide from decomposing by harmful radical pathways can be achieved through the use of the existing magnesium-derived stabilizers. This would be accomplished by enhancing the possibility of contact between it and the transition metal ions that cannot

be otherwise eliminated. Other research in the literature suggests the use of additives such as iodide ion or even certain other transition metal ions which decompose peroxide by nonharmful pathways. This research indicates that a similar effect might be achieved by using exceedingly high pressures of oxygen during certain stages of the bleach.

The analysis of the reactions which must occur during oxygen bleaching suggests that some of the potential sources of the peroxide intermediate in the pulp (especially those associated with lignin) might be eliminated through chemical or mechanical intervention. In the latter case, those peroxides and peroxide precursors which are formed during the initial reactions might be removed by extraction between the stages of a multistage oxygen bleaching sequence. Possibly even more effective would be the destruction of those substances by intermediate reactions with a powerful bleaching agent such as sodium hydrosulfite. The most elegant technique would be the addition of a suitable but unknown reagent to the bleach.

Many of the problems discussed above might be eliminated if the proper use of oxygen in the pulping and bleaching sequences were known. The pulps employed in this investigation had too little lignin. Less extreme delignification of a higher yield pulp with oxygen would probably result in greater lignin loss with less cellulose degradation. Pulps other than kraft or soda might be a more desirable raw material for oxygen bleaching because of the lignin polymerizations and radical formations which are known to occur during alkaline pulping processes. The beneficial effects of reducing partially chlorited pulps before oxygen bleaching suggest the same benefits might be achieved if incorporated into bleaching processes such as COD or CODED. It is possible

that the unsuccessful attempts of some researchers to activate the lignin of wood and pulps to oxygen with a preliminary oxidation might be successful if the harmful peroxide precursors were destroyed by reduction.

This, and the next and final report completes the initial study of oxygen bleaching which was to establish "a sufficient understanding of the process to permit judgments to be made about the extent of bleaching possible through the use of oxygen consistent with the quality of pulp obtained." The next and final report will describe multistage oxygen bleaching and will compare the effect of subsequent hydrogen peroxide and chlorine dioxide bleaching on the oxygen bleached pulps. The opportunities for process improvements and the directions of future research will be presented later on the basis of these two reports.

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APPENDIX

TABLE XXVII

SUMMARY OF DATA

	Time, min.	Pressure, psig	NaOH, %	Na_2CO_3, %	MgCO₃, %	Bleach Consist., %	1st Wash, pH	1st Wash Na_2CO_3, g./4 l.	Yield, %	Viscy. of Pulp, cps	KM-NO_4 No.	α-Cellulose	Brightness, %	Brightness Rev., %	Zero-Span Brkg. Len., km.	MIT Fold, 1 kg. tens.	Elm. Tear, g./sh.	Mullen Burst, pt.	Tensile Brkg. Len., km.	Tear Factor	Basis Wt., o.d. g./m.²	Burst Factor	Carbonyl
D-Series (base pulp)										29.0	20.5												5.92
DD	120	130	Blank		—	25.5	7.0	1.56	100.0	21.0	17.8	89.7	22.7	22.6	15.3	70	174	20.8	3.92	286	60.9	24.0	—
DE	15	130	7.10	0.24	—	25.1	9.8	4.96	92.8	5.3	7.3	83.2	39	39	8.90	8	43.6	17.0	3.86	70.4	61.9	19.3	—
DF	30	130	7.29	0.27	—	25.4	9.7	5.28	93.2	4.9	6.3	82.6	40.4	40.7	8.58	6	39.2	16.0	3.75	65.0	60.3	18.7	—
DG	60	130	6.95	0.25	—	25.2	9.5	5.96	89.6	4.7	6.2	82.3	41.5	41.7	8.61	7	39.6	15.5	3.87	64.7	61.2	17.8	—
DH	120	130	6.94	0.32	—	25.2	9.6	5.17	88.6	4.8	6.2	82.6	42.6	43.0	8.79	6	34.0	16.1	3.79	56.8	59.9	18.9	3.68
DH-Re. 1	120	130	6.94	0.32	1	25.2	9.6	5.17	88.6	4.7	6.2	82.6	42.6	43.0	8.79	6	34.0	16.1	3.79	56.8	59.9	18.9	—
DJ	15	130	3.98	0.30	—	25.6	9.2	4.72	97.8	8.9	10.8	86.6	30.2	30.6	11.80	44	79.2	22.4	4.51	128	61.9	25.4	—
DK	30	130	3.74	0.21	—	24.8	9.5	3.24	95.2	8.1	10.1	86.1	31.3	32.0	11.90	35	75.6	22.8	4.14	121	62.5	25.6	—
DL	60	130	3.87	0.21	—	24.7	9.5	3.30	95.4	8.1	9.8	86.0	31.8	32.2	12.10	38	76.4	22.0	4.15	127	60.0	25.8	—
DM	120	130	3.66	0.18	—	25.8	9.5	3.18	94.9	7.7	8.9	86.0	34.0	34.7	11.70	39	75.2	22.8	4.46	122	61.4	26.1	5.18
DN	15	130	1.83	0.19	—	26.1	9.4	2.18	99.2	18.3	15.3	89.7	23.6	24.0	14.6	54	148	23.4	3.99	245	60.4	27.2	—
DO	30	130	1.81	0.16	—	25.9	9.4	2.22	98.9	16.8	14.9	88.9	24.8	25.4	15.0	61	129	23.7	4.18	211	61.0	27.3	—
DP	60	130	1.83	0.14	—	25.2	9.4	2.08	97.8	17.1	14.2	88.5	25.6	26.1	14.4	73	130	23.3	4.17	215	60.6	27.0	—
DR	120	130	1.91	0.20	—	26.1	9.4	2.16	97.6	15.0	12.8	88.5	27.2	27.6	14.1	81	135	23.1	4.42	220	61.5	26.4	3.26
DS	120	65	6.83	0.31	1	27.7	9.5	5.03	90.2	4.9	6.7	83.3	39.4	39.3	8.62	6	44.8	14.9	3.60	73.9	60.6	17.3	—
DT	120	97.5	6.76	0.27	1	25.9	9.6	5.28	90.0	4.5	6.1	82.0	42.1	41.8	8.12	5	42.4	14.6	3.68	69.4	61.1	16.8	—
DU	120	195	6.88	0.29	1	26.3	9.3	5.36	88.7	4.3	5.3	81.4	47.6	46.9	7.69	5	38.4	14.2	3.60	63.5	60.5	16.5	—
DV	120	130	7.05	0.31	—	25.0	9.2	5.34	88.3	4.0	5.1	82.0	49.6	47.9	7.65	4	28.8	13.7	3.70	47.8	60.3	16.0	—
DW-Re. 3	120	130	7.29	0.31	—	24.7	9.4	4.20	91.3	4.0	5.3	82.0	47.8	46.3	7.62	4	29.6	13.6	3.58	49.3	60.0	15.9	—
DX	120	130	7.11	0.35	½	25.6	9.5	4.13	88.3	4.3	5.7	82.6	45.6	44.8	8.20	4	34.4	13.5	3.44	58.4	58.9	16.1	—
DY	120	130	7.19	0.34	1	25.6	9.3	5.03	87.4	4.3	5.8	82.8	44.4	43.9	8.50	5	40.8	15.2	3.60	67.9	60.1	17.8	—
DZ[a]	120	130	8.39	1.00	—	26.1	9.7	4.07	88.6	4.7	6.1	83.1	45.5	45.7	8.44	7	48.4	15.6	3.54	79.0	61.3	17.9	—
E-Series																							
EA	120	130	7.51	0.28	—	26.1	9.8	3.53	90.0	4.7	--	85.2	88.4	87.0	8.5	5	53.2	11.2	2.79	92.8	57.3	13.7	--
EB	120	130	3.72	0.16	—	25.9	9.3	2.62	96.8	7.8	--	86.0	86.9	85.9	11.5	13	102	13.6	3.10	177	57.5	16.6	--
EC	120	130	1.84	0.12	—	26.4	9.4	1.77	99.2	9.6	--	86.0	85.7	84.5	12.8	15	135	15.6	3.19	229	58.9	18.6	--
ED	120	130	Blank		—	27.1	7.0	0.89	100.3	13.2	—	—	85.6	83.8	13.6	12	144	14.0	2.89	248	58.1	16.9	—
F-Series																							
FA	120	130	7.30	0.25	--	26.4	11.8	2.33	97.5	4.7	--	--	--	--	--	--	--	--	--	--	--	--	--
FB	120	130	3.51	0.14	—	26.0	10.2	2.08	94.8	5.0	--	--	--	--	--	--	--	--	--	--	--	--	--
FC	120	130	1.81	0.12	—	25.8	9.4	1.79	99.6	6.5	--	--	--	--	--	--	--	--	--	--	--	--	--
FD	120	130	Blank		—	27.0	8.3	1.10	100.1	11.8	—	—	—	—	—	—	—	—	—	—	—	—	—
FE	120	130	8.27	0.31	1	25.6	12.2	1.91	101.0	8.9	—	99.0	89.2	89.3	—	—	—	—	—	—	—	—	—
FF-Re. 1	120	130	8.35	0.36	1	26.5	12.2	1.54	97.2	8.1	—	98.7	89.5	89.7	—	—	—	—	—	—	—	—	—
G-Series (base pulp)										21.0	1.2												
GA	120	130	7.34	0.29	--	25.1	9.6	3.78	94.2	3.6	—	—	87.1	85.4	7.7	3	32.0	11.9	3.31	54.3	58.9	14.2	--
GB	120	130	3.87	0.15	—	25.4	9.4	2.78	97.7	5.6	—	—	84.6	83.5	10.0	11	58.8	15.9	3.67	100	58.6	19.1	—
GC	120	130	1.97	0.13	—	25.8	9.2	1.75	100.8	8.2	—	—	81.6	80.9	12.8	21	102	18.2	3.79	171	59.6	21.5	—
GD	120	130	Blank		—	25.5	7.5	0.58	102.2	13.1	—	—	77.6	76.7	14.4	40	172	21.7	3.87	287	59.9	25.5	—

See end of table for footnotes.

TABLE XXVII (Continued)

SUMMARY OF DATA

	Time, min.	Pressure, psig	NaOH, %	Na_2CO_3, %	MgCO₃, %	Bleach Consist., %	1st Wash, pH	1st Wash, Na_2CO_3, g./4 l.	Yield, %	Viscy. of Pulp, cps	KM-NO₄ No.	α-Cellulose	Brightness, %	Brightness Rev., %	Zero-Span Brkg. Len., km.	MIT Fold, 1 kg. tens.	Elm. Tear, g./sh.	Mullen Burst, pt.	Tensile Brkg. Len., km.	Tear Factor	Basis Wt., o.d. g./m.²	Burst Factor	Carbonyl
H-Series (base pulp)										26.2	13.0												
HA	120	130	7.71	0.33	—	25.8	9.9	4.20	90.7	5.9	3.7	84.6	59.9	60.2	10.4	12	78	14.8	3.24	128	61.1	17.0	—
HB	120	130	3.75	0.20	—	25.9	9.5	2.83	95.8	10.6	4.8	84.5	50.1	50.8	13.1	26	132	18.0	3.52	221	59.8	21.2	—
HC	120	130	1.97	0.21	—	26.8	9.2	1.70	96.2	18.3	6.6	83.3	43.0	43.4	13.9	33	159	17.4	3.54	267	59.6	20.5	—
HD	120	130	Blank		—	28.0	7.0	1.04	98.9	19.8	11.2	86.6	32.1	31.8	14.6	20	150	14.9	3.14	253	59.2	17.7	—
J-Series (base pulp)										26.6	6.5												
JA	120	130	7.59	0.31	—	25.8	10.4	3.24	92.5	6.8	1.6	86.3	72.0	71.6	10.7	16	93.2	15.0	3.21	154	60.5	17.4	2.33
JB	120	130	3.75	0.22	—	26.2	9.6	2.51	96.6	12.3	2.1	87.7	63.5	63.4	13.6	34	162	18.2	3.63	266	60.9	21.0	—
JC	120	130	1.78	0.13	—	26.5	9.2	1.64	98.6	19.1	2.7	87.2	58.4	58.2	14.3	39	154	19.4	3.73	258	59.6	22.9	—
JD	120	130	Blank		--	26.2	6.9	0.69	97.1	18.7	4.4	88.1	44.2	44.1	14.6	42	158	18.8	3.72	260	60.7	21.8	7.24
JE	120	130	7.06	0.29	1	25.8	11.8	2.43	94.3	11.6	1.6	86.7	75.2	74.5	12.4	14	136	14.2	3.17	231	58.9	16.9	—
JF	120	130	6.83	0.37	1	26.2	10.6	2.76	93.6	6.3	1.4	86.9	73.5	72.9	10.5	14	92.8	14.4	3.18	150	61.7	16.4	—
K-Series (base pulp)										30.5	20.1	92.0											
KA	60	130	6.90	0.24	1	26.0	10.7	4.59	94.4	14.4	6.2	86.6	43.0	43.5	13.3	23	143	20.7	3.26	238	60.1	20.7	—
KB	120	130	6.82	0.30	1	25.8	9.9	6.19	93.4	13.6	6.6	86.7	45.4	45.8	13.6	25	136	18.5	3.38	226	60.3	21.6	--
KB-Re. 1	120	130	7.34	0.35	1	25.4	10.0	5.26	93.4	11.5	6.4	87.5	45.4	45.9	13.9	47	154	20.6	3.63	252	61.1	23.6	—
KC	120	130	6.94	0.34	1	26.0	9.8	6.79	91.6	11.9	8.6	86.8	43.9	43.9	12.7	28	134	17.5	3.37	226	59.3	20.7	—
KD	120	130	3.54	0.18	1	25.9	9.4	5.09	100.5	17.0	8.1	86.9	38.0	38.3	14.3	38	146	20.7	3.64	243	60.2	24.2	—
KE	15	130	7.14	0.33	1	26.1	11.7	3.28	95.4	15.3	7.6	86.9	36.4	37.2	13.4	33	149	18.0	3.56	243	61.2	20.7	—
KF	120	130	1.68	0.15	1	26.5	8.9	3.06	99.5	22.2	13.8	89.0	28.6	29.2	14.7	27	158	17.8	3.39	260	60.8	20.6	—
KG	30	130	7.24	0.30	1	25.8	11.2	3.72	95.5	14.6	8.1	86.7	39.4	40.3	13.9	21	140	17.2	3.44	238	58.7	20.7	—
KH	120	130	—	--	1	26.5	7.0	0.79	100.0	--	18.6	90.5	25.6	25.6	13.9	12	136	13.4	2.82	228	59.6	15.8	—
KJ	120	130	6.66	—	1	25.8	10.6	4.26	95.2	11.3	6.2	86.7	47.2	47.9	12.9	16	140	15.9	3.21	231	60.5	18.5	—
KK	120	130	6.74	0.29	1	26.0	10.2	6.30	94.6	13.6	6.7	87.1	49.0	49.3	14.2	30	147	19.6	3.68	246	59.8	23.0	—
KL-Re. 1	120	130	7.00	0.36	1	25.9	10.2	6.94	92.3	13.9	6.4	87.3	48.4	48.5	13.7	23	149	18.9	3.65	243	61.2	21.7	—
KM	120	148	1.67	—	1	24.6	10.4	1.70	93.4	16.6	18.0	88.8	27.0	27.0	14.0	16	132	14.6	3.07	212	62.2	16.5	—
KN	120	130	6.68	0.26	1	26.4	9.7	4.88	87.8	7.6	5.0	85.4	49.2	48.7	12.4	21	116	17.0	3.59	192	60.4	19.8	—
KO	120	130	6.56	0.15	1	25.8	10.5	4.68	94.4	14.7	6.1	84.6	49.8	50.2	14.1	31	165	18.8	3.69	267	61.8	21.4	—
KP	120	195	7.15	0.24	1	25.5	9.7	6.00	91.9	13.5	6.0	86.9	47.2	47.9	13.6	34	161	18.4	3.78	268	60.1	21.5	—
KP-Re. 1	120	195	7.00	0.25	1	26.3	9.6	6.02	92.1	12.5	5.9	87.0	47.6	48.1	13.2	38	154	19.5	3.86	257	59.9	22.9	—
KQ	120	97.5	6.76	0.21	1	26.0	9.6	5.61	91.8	14.1	7.0	86.9	43.3	43.7	13.7	42	143	18.6	3.97	242	59.0	22.2	—
KR	120	65	6.92	0.24	1	26.2	10.2	4.76	93.7	13.0	6.9	88.1	41.8	42.9	14.2	41	135	19.8	3.76	229	59.0	23.6	—
KS	120	130	7.32	0.35	—	25.4	10.0	2.82	91.6	10.3	6.2	87.8	51.3	49.7	12.9	33	118	19.9	3.83	196	60.3	23.2	—
KT	120	113.75	7.21	0.34	1	26.2	9.9	5.34	93.2	13.5	6.6	88.5	45.3	45.6	14.0	47	141	20.5	3.81	236	59.9	24.1	—
M-Series (base pulp)										32.0	19.5	90.1	25.0	24.6	14.1	6	170	23.2	4.03	283	60.0	27.2	—
MA	120	130	7.05	0.30	1	25.2	9.3	5.26	91.7	6.4	5.3	84.2	48.7	48.7	10.2	22	68.4	21.6	—	116	58.9	25.8	
MB	60	130	7.01	0.31	1	26.6	9.7	4.66	91.8	6.8	6.3	85.2	44.5	43.8	11.1	—	—	—	—	—	—	—	—
MC	30	130	6.77	0.25	1	25.6	10.1	4.26	98.4	7.5	6.6	85.7	43.3	42.2	11.4	—	—	—	—	—	—	—	—

[a] DZ contained 0.287 Mg acetate instead of $MgCO_3$.

Note: D-Series = unbleached Champion southern pine kraft (high transition metal content).
E-Series = bleached Champion southern pine kraft (prepared by Champion).
F-Series = Hercules PS-57 cotton linters.
G-Series = Champion southern pine kraft (fully bleached with $NaClO_2$).
H-Series = Champion southern pine kraft (partially bleached with $NaClO_2$).
J-Series = Champion southern pine kraft (partially bleached with $NaClO_2$).
K-Series = unbleached Champion southern pine kraft (low transition metal content).
M-Series = unbleached Champion southern pine kraft (medium transition metal content).

Abbreviations used in this table are as follows: consist. = consistency; viscy. = viscosity; rev. = reversion; brkg. = breaking; len. = length; tens. = tension; sh. = sheet; Elm. = Elmendorf.